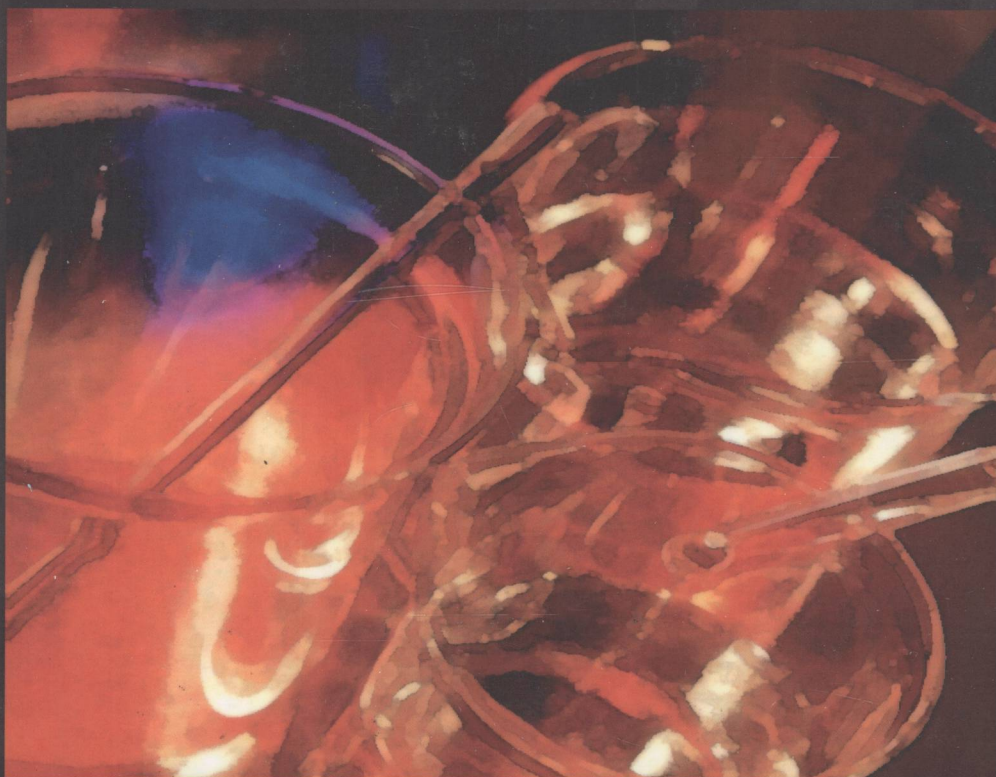


INORGANIC POLYMERS



Roger De Jaeger and Mario Gleria
Editors

NOVA

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ROGER DE JAEGER
AND
MARIO GLERIA
EDITORS



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INORGANIC POLYMERS

*To Monique, To Carla, Luca, Fabio, and to all those
we hold dear for their love and patience*

PREFACE

After the initial success of the first book we edited in 2004 titled: “Phosphazenes: A Worldwide Insight”, we devoted our interest to a second editorial venture mostly dedicated to inorganic macromolecules. The reason for this fact was dictated by the increasing scientific interest and the enhanced possible industrial and technological applications of these substrates.

This book on “Inorganic Polymers” collects contributions coming from the most scientifically developed countries in the world (Europe, USA and Japan), written by eminent scientists on their own research topics. Thus, silicon-based inorganic polymers were treated by M Cypryk (Poland), G. Kickelbick (Austria), X. Coqueret (France), A. Colas (Belgium), J. Koe (Japan), W. Uhlig (Switzerland), and by M. Rehahn and M. Weinmann (Germany). Different aspects of phosphorus-containing macromolecules were described by F.F. Stewart (USA), R. De Jaeger and L. Montagne (France), and by M. Carenza, S. Lora, and M.Gleria (Italy). Tin- and germanium-based polymers were illustrated by M. Okano (Japan), while inorganic dendrimers were presented by A.M. Caminade and J.P. Majoral (France) and by V. Balzani (Italy). Miscellaneous topics covering the flame-retardant and the intumescent behavior of the inorganic macromolecules (S. Bourbigot, France), ionically-conductive inorganic macromolecules (E. Montoneri, Italy) and chiral inorganic polymers (G.A. Carriedo and J.F. Garcia-Alonso, Spain) were also addressed.

This book does not pretend to be exhaustive, but we feel that it is wide enough to cover the most important and representative topics in the field of inorganic polymeric materials, providing a reasonable scientific view of this domain both to newcomers and to scientists already active in specific areas.

We are deeply indebted to all the scientists that accepted to join us in this venture in an enthusiastic way and contributed to this book, making it possible.

Roger De Jaeger and Mario Gleria

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Chapter 1

GENERAL REVIEW ON POLYSILOXANE SYNTHESIS

Marek Cypryk

Center of Molecular and Macromolecular Studies,
Polish Academy of Sciences, Sienkiewicza 112,
90-363 Łódź, Poland

ABBREVIATIONS

All silicones in the text are composed of, or contain some, or all, of the four basic units:

M (monofunctional) $\equiv \text{R}_3\text{Si}(\text{O})_{1/2}$

D (difunctional) $\equiv \text{R}_2\text{Si}(\text{O}_2)_{1/2}$

T (trifunctional) $\equiv \text{RSi}(\text{O}_3)_{1/2}$

Q (tetrafunctional) $\equiv \text{Si}(\text{O}_4)_{1/2}$

T and Q units constitute parts of many highly branched oligomers and polymers, or crosslinked networks.

For the most common siloxanes, polydimethylsiloxanes, $\text{R} = \text{Me}$;

Thus permethyl cyclic siloxanes would be referred to as D_n , e.g. D_3 , D_4 , D_5 , ...

Linear oligomers are often called MD_nM , e.g. MM, MDM, MD_2M , ...

$\text{D}^{\text{H}} = \text{MeHSi}(\text{O})_{1/2}$; for example, $\text{D}^{\text{H}}_4 \equiv$ tetramethylcyclotetrasiloxane (MeHSiO)₄

V = $\text{MeViSi}(\text{O})_{1/2}$

P = $\text{PhMeSi}(\text{O})_{1/2}$

F = $\text{Me}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{Si}(\text{O})_{1/2}$

DDS = dimethyldichlorosilane

List of abbreviations used for polymer identification:

PDMS = polydimethylsiloxane

PMHS = polymethylhydrosiloxane, or polymethylsiloxane

PDHS = polydihydrosiloxane, or polysiloxane

PMES = polymethylethylsiloxane

PDES = polydiethylsiloxane

INTRODUCTION

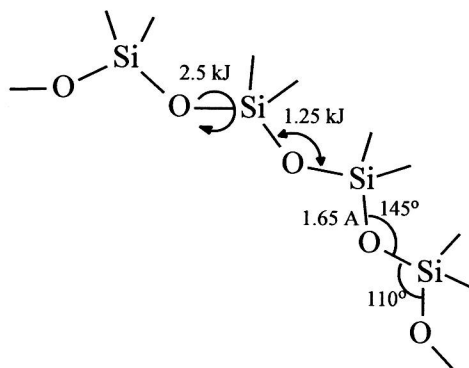
It was probably Albert Ladenburg who obtained silicone oil for the first time in 1872 [1]. However, the prospects for development of this area of chemistry seemed poor until the 1940's, when the commercial process for the preparation of silicone precursors was invented independently by Rochow in the US and Muller in Germany. Since that time, thousands of papers and patents on the synthesis of polysiloxanes have appeared. Among them there are excellent books and reviews, to which the reader is referred for more comprehensive information [2-18].

The commercial success of polysiloxanes is due to their unique properties, which cannot be easily matched by organic replacements. The constantly expanding production and applications of polysiloxanes, in particular, their growing use for the design and synthesis of various well defined macromolecular architectures, call for a deeper knowledge of the polysiloxane chemistry.

The purpose of this review is to give a general summary of the state of art in the polysiloxane synthesis. An emphasis has been put on the synthesis of linear polysiloxanes, although three-dimensional (3D) branched and dendritic macromolecular structures are also briefly reviewed.

THE ELECTRONIC STRUCTURE OF THE SILOXANE BOND

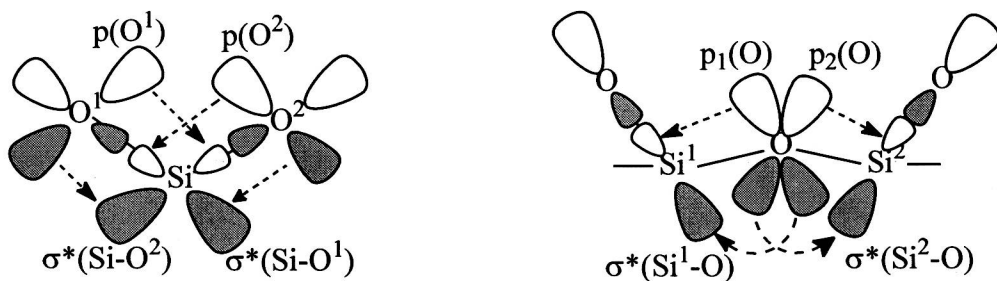
Electronic character of the siloxane bond has a great impact on the reactivity and physical properties of polysiloxanes. The siloxane bond, Si-O, is considerably shorter than what would be expected from simple additivity of the atomic radii of silicon (1.17 Å) and oxygen (0.66 Å). Hence, this linkage is more complex than a regular σ bond. A large difference in electronegativities of the constitutive silicon and oxygen atoms, which, according to Pauling scale, are equal to 1.8 and 3.5, respectively, results in partially ionic character, estimated to 40%-50% on the basis of empirical calculations [19].



Scheme 1.

The Si-O bond distance shortening suggests a partial double bond character of Si-O. In earlier literature, it was interpreted in terms of the $[\text{p}(\text{O}) \rightarrow \text{d}(\text{Si})]_{\pi}$ interaction [3]. Indeed,

there are several arguments supporting this hypothesis. Siloxanes are much weaker bases than ethers, which is in accord with the concept of delocalization of the lone pair of electrons from oxygen to the empty d orbitals of silicon. The SiOSi chain is extremely flexible. The SiOSi angle, ranging usually from 140° to 180° , is much wider than the tetrahedral angle [3]. The barrier of rotation around the Si-O bond of 2.5 kJ/mol in $(\text{Me}_3\text{Si})_2\text{O}$, as well as the barrier of linearization of the SiOSi angle, ca. 1.3 kJ/mol, are very low [20]. This again is in agreement with the spatial arrangement of the d orbitals. Recent theoretical calculations show, however, that the contribution of the d orbitals at Si to the total electron distribution is small [21]. Many authors prefer to interpret these features as a consequence of the strongly ionic character of the Si-O bond and of the negative hyperconjugation $[\text{p}(\text{O}) \rightarrow \sigma^*(\text{Si-X})]_\pi$ (also referred to as the anomeric effect, Scheme 2) [15,21]. The interaction is particularly strong when X is an electronegative atom, e.g., N, O, F. As the other authors indicate, the $(\text{p-d})_\pi$ concept cannot be totally abandoned, because the theoretical calculations did not provide unequivocal information on the character of the Si-O bond [22]. Calculations suggest that the $(\text{p-d})_\pi$ interaction plays an important role at least in the siloxane species having enhanced electron density on oxygen, such as silanolate anions and silanols hydrogen-bonded to a base [23].



Scheme 2.

REACTIVITY OF THE SILOXANE BOND

General reactivity of the siloxane bond is largely a function of its electronic properties. Thus, in view of theoretical results, low basicity of siloxane oxygen is mainly due to the electron delocalization (by negative hyperconjugation or p-d back donation) along the OSiO (silaacetal) linkage. Electron delocalization and contribution from ionic structures are also responsible for an extra strengthening of the siloxane bond [15,21,24]. High energy of the siloxane bond, (estimated to fall in the range of 450 kJ/mol [25] to 570 kJ/mol [26]), makes it very resistant to homolytic cleavage. On the other hand, the siloxane bond is strongly polarized. Moreover, the silicon atom has a relatively large size and the substituents appear only at every second atom in the chain. In connection with the high flexibility of the chain, these features account for the relatively low steric hindrance and high accessibility of silicon to a nucleophilic attack. This results in relatively high reactivity of the siloxane bond toward heterolytic cleavage [3].

PROPERTIES AND APPLICATIONS

There is a huge bibliography concerning properties and applications of polysiloxanes and siloxane-derived materials [2-14,14-16,16-18,27-30]. Detailed presentation of this area is not a subject of this review. The main points are only shortly marked to show the relationship between the electronic structure of the siloxane and silacetal bonds and the macroscopic

Thermal and Chemical Stability

As expected from the high values of bond energies, silicones, in the absence of acids or bases, are exceptionally thermally stable. Degradation of polydimethylsiloxane begins at about 350 °C. In inert atmosphere, the main products are low molecular weight (MW) cyclosiloxanes. Phenyl groups improve thermal stability of silicones [6,7,31,32]. Silicones are also resistant to oxidation and exhibit good flame retardancy [7,13,32]. They are stable toward hydrolysis (except extreme pH conditions) and toward typical organic solvents [2,3].

Elastomeric Properties

Unusual mobility of the siloxane chain is a consequence of the electronic structure of SiOSi linkage and of the small steric hindrance of side groups due to the relatively long distance between them, as they occur at only every second atom in the backbone. On the other hand, nonpolar side groups like methyls effectively shield the polar SiO backbone, which results in the weak intra- and intermolecular forces in polysiloxanes. These features are manifested in low viscosity of polysiloxanes up to high molecular weight and in pronounced elasticity of polymers at low temperatures. Glass transition points for PMES, PMHS and PDES are the lowest of all common polymers [32].

Weak intermolecular forces are responsible for poor mechanical properties of polysiloxanes. However, by cross-linking of the chains as well as by reinforcement of silicone materials with resin or a filler, their mechanical properties can be significantly improved, making them applicable as elastomers in the exceptionally wide temperature range. Silicone rubbers can remain flexible at temperatures as low as -100 °C yet perform satisfactorily at temperatures over 200 °C [33-35].

Surface Properties

Polar inorganic siloxane backbone surrounded by nonpolar pendant organic groups gives amphiphilic character to polysiloxane. High mobility allows the polysiloxane chain to easily adapt the most thermodynamically favored conformation at the interface. This feature interplaying with the exceptionally weak interactions between side groups give them extremely low surface tension [25,36,37]. Silicone fluids spread easily over the surfaces of various substances, and are thus widely used as water repellents, foam controllers, lubricants, surfactants and ingredients for cosmetics. By combination with hydrophilic fragments, the

surface activity of silicones may be modified in a wide range making them applicable in even seemingly contradictory roles, from release coatings to excellent adhesives (such as pressure-sensitive ones), from anti-foaming agents to foam stabilizers, etc. [7,13,18,25,37].

An important consequence of the low intermolecular forces in polysiloxanes is also the exceptional gas permeability of silicones [25].

Dielectric Properties

Silicones exceed all comparable materials in their insulating properties as well as in the flexibility in electrical applications. They are non-conductive because of their chemical nature and maintain dielectric strength in temperature extremes far higher or lower than conventional materials can handle. Exposure to heat, cold, moisture, oil, and ozone does not significantly change their electrical properties. Thus, when compounded with the proper fillers and additives, are used to produce rubber for a wide range of electrical insulating applications. Very low dielectric permittivity in the range of 2.4-2.75 as well as high dielectric strength (13.7-15.8 kV/mm) and volume resistivity (about 1×10^{15} ohm·cm at 20 °C) of methylsilicones make them excellent materials for insulating purposes [38].

Biocompatibility

Very important feature of silicones is their biological inertness, due to their hydrophobicity and chemical stability. They are odorless and tasteless, do not support bacteria growth, and will not stain or corrode other materials. Most importantly, silicone rubbers exhibit superior compatibility with human tissue and body fluids. They are essentially non-toxic and therefore are widely used for cosmetics and medical applications [18,39].

High Technology Applications

Silicon-based nanomaterials have potential as the “material of choice” for numerous applications in photonics, electronics, energy, and biology. For instance, silicone-poly(oxyethylene) copolymers form vesicles, which can function not only as encapsulants and delivery agents of active ingredients but also as nanoreactors. Microemulsions and liquid crystals formed from silicone surfactants have been used to enhance delivery of personal care products and to direct synthesis through templating of mesostructured materials. Silicone-organic copolymers self-assemble to ordered or disordered phases, which control the physical and mechanical properties of the polymeric system and facilitate the stabilization of multiphase-component emulsions.

The rapid development of thermotropic oligosiloxane liquid crystalline (LC) materials is associated with their promising potential. Oligosiloxane functionalization can be used to tune the properties of mesogens. The oligosiloxane component tends to induce microphase segregation, thus ordered phases (such as lamellar structures) are readily observed. This

technology finds applications in the liquid crystal display market and in other electro-optics opportunities [40-42].

Functional Silanes - Precursors to Polysiloxanes

Functional silanes of the general formula $R_{4-n}SiX_n$, where X is Cl, OR, OC(O)R, NR_2 or other hydrolysable group, are the precursors for the polysiloxane synthesis. The most common precursor of polydimethylsiloxane is Me_2SiCl_2 (DDS). Since the organosilicon compounds do not appear in nature, all the polysiloxane monomers must be obtained synthetically. The methods of their preparation have not changed significantly since the beginning of production. The natural source of silicon is silica (SiO_2). Silica is reduced to elemental silicon with carbon in the high temperature electro-thermic reduction [4,43]. Silicon is then transformed into organosilicon species, most often by one of the following methods:

1. Reaction of organic compounds with silicon at elevated temperatures. This is the industrial route to methylchlorosilanes, called the "Direct Process" [15,43,44].
2. Chlorination of silicon and a subsequent substitution of some chlorine atoms by organic groups with organometallic reagents, such as organolithium compounds, Grignard reagents, organic zinc compounds and others [45].
3. Transformation of silicon into silyl hydrides and a subsequent addition to multiple bonds in a hydrosilylation process [46-48].

Dimethyldichlorosilane (DDS), the most important substrate for the silicone industry, is synthesized in the so-called Direct Process, which involves the reaction of gaseous methyl chloride with a contact mass of silicon containing copper as catalyst in continuously operating fluidized or stirred bed reactors at 250-300 °C [44]. The yield of DDS can reach more than 90%. The other products are methylchlorosilanes, Me_nSiCl_{4-n} , $n = 0-4$, in addition to a few percent of disilanes. The way of preparation of contact mass, the purity of the silicon and the conditions of the process strongly affect the product composition. Addition of Cl_2 to the feed increases the proportion of $MeSiCl_3$ and $SiCl_4$, while introduction of HCl or H_2 gives rise to the Si-H containing products. The use of other alkyl or aryl halides (ethyl chloride, vinyl chloride, allyl chloride, chlorobenzene) leads to the corresponding organohalosilanes, R_nSiX_{4-n} .

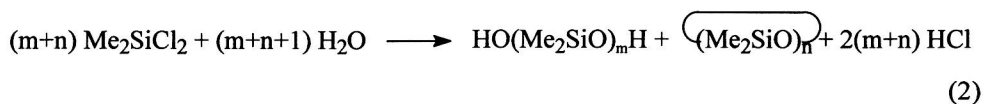


An effort continues to improve an overall yield of the desired products of the direct process through the understanding of the mechanism of component reactions, of the effect of promoters and additives and of the silicon morphology [49]. The reactions of silicon with alcohols, leading to methoxysilanes are also exploited [50,51].

The literature on the synthesis of polysiloxane precursors containing hydrolysable functions other than halogen at silicon is very rich, including numerous important monographs and reviews [2,3,15,17].

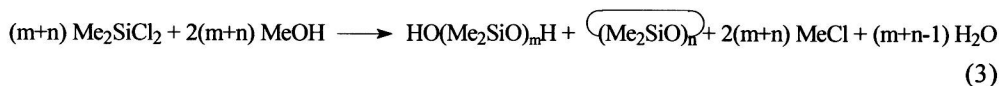
Industrial Synthesis of Polysiloxanes

The general route to linear polysiloxanes from silicone monomers used in the industry is a two step process. The first step is a hydrolytic polycondensation of the bifunctional silane precursor (most often DDS). This process leads to a mixture of linear and cyclic oligosiloxanes, frequently referred to as the hydrolyzate. With DDS, the reaction occurs according to general equation 2.



The ratio of cyclic to linear oligomers can be varied by changing the reaction conditions (water/silane ratio, reaction time, temperature, the presence of additives).^{2,5,10,16} For example, rapid removal of HCl from the reaction mixture leads almost exclusively to short-chain siloxanediols. Cyclic oligomers comprising up to 2/3 of total product can be obtained after prolonged contact with HCl. Further increase of the yield of cyclics can be achieved when they are separated from the reaction mixture by vacuum distillation. The second step is a transformation of the oligomers into a high molecular weight polymer. The synthesis of the high polymer is performed either by a polycondensation of the hydroxy-terminated, low MW polysiloxanes (α,ω -polysiloxanediols) or by a ring opening polymerization of cyclic oligomers.

The methanolysis process is a potentially interesting alternative to hydrolytic polycondensation. This process allows for a direct recovery of chloromethane from methylchlorosilanes, according to equation 3 [10,16].



POLYSILOXANES BY POLYCONDENSATION ROUTES

Hydrolytic Polycondensation of Chlorosilanes

The hydrolytic polycondensation may be presented as a set of reversible reactions (equations 4-7).





Thermodynamics of the overall reaction (equation 7) is very favorable for siloxane formation. The enthalpy of hydrolysis/condensation of trimethylchlorosilane in the gas phase, deduced from bond dissociation enthalpies (BDE), is ca. -21 kJ/mol. (BDE's for silicon compounds were taken from ref. [26,52,53]; BDE's for H₂O and HCl were taken from ref. [54]). The enthalpy of this reaction in water was measured to be as large as -46 kJ/mol to -52 kJ/mol. The hydrolysis/condensation of Me₂SiCl₂ is even more exothermic, $\Delta H^{298} = -134.3$ kJ/mol [55,56]. Comparison of the enthalpy values for the reaction in gas and condensed phases indicates, that a large amount of heat produced in hydrolysis is due to the HCl hydration. Equilibrium constant for aqueous hydrolysis of Me₃SiCl in constant volume conditions was estimated to about 9×10^{12} [57]. These data suggest that the reaction should proceed to virtually full conversion of chlorosilane. However, it was shown that some amount of SiCl may remain unhydrolyzed when saturated aqueous HCl is in equilibrium with the final hydrolysis products, due to the fact that the thermodynamic activity coefficient for HCl in concentrated HCl solution is very high, while that for H₂O is low [58]. Thus, the overall energy and equilibrium position of this process strongly depends on the water/silane proportion, on the polarity of the medium and its ability to hydrogen bonding. The studies on hydrolytic condensation in the gas phase have also shown incomplete conversion of alkylchlorosilanes [59].

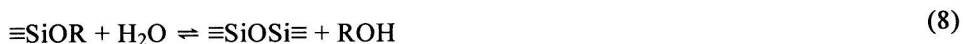
Kinetic data for the hydrolytic polycondensation of DDS in solution indicate that fast hydrolysis is followed by the slower, rate-controlling condensation. The overall reaction rate decreases strongly in order SiCl₄ > RSiCl₃ > R₂SiCl₂ > R₃SiCl. [60]. The intermediate hydroxychlorosilanes are very unstable. Nevertheless, they have recently been observed by NMR in hydrolytic polycondensation of SiCl₄ [61].

Products of the hydrolytic polycondensation process depend on the SiCl/H₂O proportion. If water is used in excess, the products are hydroxy-terminated short chain polysiloxanes and cyclic siloxanes. In deficiency of water, the main products are chloro-terminated oligosiloxanes. However, formation of cyclics cannot be completely eliminated due to the fast functional group exchange (equation 4) [62].

Hydrolytic polycondensation, when carried out in a large excess of water, probably occurs via homofunctional silanol condensation (equation 6), which is effectively catalyzed by HCl protonating the SiOH group. On the other hand, the heterofunctional polycondensation (equation 5) may become important in the hydrolytic polycondensation of DDS carried out with concentrated HCl solution in a heterogeneous system, where the thermodynamic activity of H₂O is low and that of HCl is very high. The heterofunctional reaction dominates when hydrolytic polycondensation is performed in the presence of bases [63].

Hydrolytic Polycondensation of Alkoxysilanes

Alkoxysilanes are the useful alternative to chlorosilanes in hydrolytic polycondensation processes. Their advantage is that they are more chemically stable than chlorosilanes and the by-product of hydrolysis, alcohol, is low toxic, non-aggressive and non-corrosive, compared to HCl. The reactions of alkoxysilanes Si(OR)_4 and R'Si(OR)_3 with hydroxy-terminated polysiloxanes are extremely important for the preparation of polysiloxane networks, particularly in sol-gel processes [8,15,64,65]. Reaction 8 was also used for the synthesis of linear polymers, in particular, block copolymers [66-69]. This reaction is useful for the synthesis of polysiloxanes containing basic side groups [69].



The process is very complex and sensitive to many factors: silane concentration, amount of water and alcohol, the type and concentration of catalyst, solvent and temperature. A variety of catalysts are used to promote this process: CF_3COOH , [69,70] tin(II) carboxylates, [71-74] phosphazanium salts, [75] alkaline earth metal oxides, [76] and uncharged bases (amines) [66,67]. Heterofunctional condensation competes with the silanol homocondensation. Their relative rates vary with the reaction system. Polycondensation is accompanied by an SiOH-SiOR end group exchange resulting from fast hydrolysis and alcoholysis reactions [77,78]. The specific rates of these reactions are often much higher than those of polycondensation [70]. The $\text{SiOR} + \text{SiOH}$ polycondensation is the equilibrium process. A reverse reaction, i.e., alcoholysis of various siloxanes $(\text{XMe}_2\text{Si})_2\text{O}$, was studied in acidic systems [79].

Tin(II) carboxylates, e.g., stannous octoate, are very effective catalysts of the $\text{SiOR} + \text{SiOH}$ polycondensation [71,74]. In some systems the process is very selective towards heterofunctional condensation, as it has been demonstrated for the reaction of α,ω -dihydroxypolydimethylsiloxane with tetraethoxysilane [80]. In contrast, the condensation of α,ω -dihydroxypolydimethylsiloxane with methoxytrimethylsilane was accompanied by a significant chain extension [71].

A comparison of the activities of various catalysts in the condensation of silanols with alkoxysilanes led to the concept of bifunctional catalysis, in which the catalyst acts both as an acid and a base [81]. Possible structures of the transition states, when carboxylic acid and hydroxylamine are used as catalysts are shown as structures 1 and 2, respectively.

