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The Technology, Structure, and Properties of Organosilicon Dielectrics-polyorganosilasesquioxanes

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The available information about the technology of the preparation of polyorganosilasesquioxanes, their structure, and properties is described systematically, surveyed, and compared with that on inorganic oxide dielectrics. The possibilities and advantages of their application as dielectric materials in semiconductor electronics are examined; analysis of the experimental literature data has led to the conclusion that the method of preparation has a decisive influence on the mechanism of the formation of oligomer molecules their conversion into polymers, and their interaction with various supports.
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I. INTRODUCTION

The development of the leading branches of the national economy such as power engineering, electronics, computer technology, electrical engineering, radioengineering, instrument making, etc. is linked directly to the accelerated incorporation in industry of new physical principles and expansion of the applications of those already known. This is possible solely on the basis of materials with characteristics conforming to the maximum extent to their functional purpose[1].

One of the most widely used materials in modern electronic engineering is single crystal silicon[2,3], on the basis of which a whole range of semiconductor devices has been created. The importance of silicon as a general purpose semiconducting material will not diminish in the future. Following the expansion of the assortment of special purpose semiconductors such as compounds of the type $A^{III}B^{V}$, $A^{I}B^{V}$, $A_2^{II}B^{IV}$, $A^{II}B^{V}$, $A^{II}B^{VI}$, oxides, chalcogenides, ternary and more complex inorganic compounds[2,3], and organic semiconductors[1,4], silicon will be employed still more vigorously and economically in electronic structures where its useful properties are most fully realised.

II. DIELECTRIC MATERIALS IN ELECTRONIC INSTRUMENT MAKING

The necessity to employ dielectric materials in the manufacture of semiconductor instruments[3,5] and integrated circuits is generally known. In metal–dielectric-semiconductor metallic structures (MDS structures) or, as a special case, metal–oxide–semiconductor structures (MOS structures), the dielectrics are active structural elements. Furthermore, oxide dielectrics are used in the technology of semiconductor instrument making as masks in thermal diffusion or ion beam doping processes[6-8]. Amorphous silicon dioxide, formed either by the thermal oxidation of the surface of a single crystal[9,10] or by the decomposition of organosilicon compounds, for example, pyrolysis, hydrolysis, or treatment in a glow discharge plasma[11-13], is widely used in silicon devices. The influence of the conditions of preparation on the quality of amorphous silicon dioxide films has been examined[14-17] and the dependence of the electrical strengths of the films obtained by different methods (thermal oxidation in dry oxygen, high-frequency and reactive deposition) on the method of preparation has been established[15]. As in prolonged annealing in an atmosphere of nitrogen at temperatures in the range 250–500 °C,[14] an increase of the defectiveness of the film is due to the development of pores all the way through the film and the formation of microcrystallites in the amorphous dielectric. The processes involved in the preparation of silicon and titanium oxides without carbonaceous impurities (the limiting impurities for a dielectric on the surface of silicon in view of the possible carbidisation) by the hydrolysis of the corresponding tetraethoxy-derivatives have been subjected to thermodynamic analysis[16] and the process conditions have been determined.

The influence of the properties of amorphous silicon dioxide on the parameters of silicon MOS structures has been examined in detail in a number of studies[10,18-35]. Analysis of the results[19-21,32,33,35] has led to the concept of the structure of the silicon single crystal–amorphous SiO_2 system illustrated in Fig.1, from which one can see the complex structure of the transition layer incorporating both the material of the single crystal, as a result of the dissolution of oxygen in the surface regions and the formation of additional surface and interphase[35] states of different kinds, and to an even greater extent the material of the amorphous dielectric particularly near the interface. The amorphous SiO_2 on the surface of a silicon single crystal is distinguished by a pronounced layer inhomogeneity and undergoes a series of phase transitions depending on the distance from the interface.

Region I (Fig. 1) of amorphous SiO_2 (distance up to 10 Å), incorporated in the transition layer, is characterised by the non-stoichiometry of the oxide[19,21,22,33] and the presence of incomplete hydrated and distorted silicon–oxygen tetrahedra[19]. It is followed by region II (between 10 and 30 Å), consisting of amorphous material with a pseudo-coesite structure, which is due to the operation of compressive forces (the compensating stretching forces act on the silicon single crystal). The relaxation of the internal stresses[22,31] in the $Si–SiO_2$ system, which occurs mainly in this region, leads to local breaks in the continuity of the layer. It is significant[31] that, regardless of the oxidation conditions, the grown oxide may be metastable and the structural mechanical stresses in it do not relax fully. Region III is a zone of the phase transition[20] from the non-equilibrium pseudo-coesite structure to the pseudotridymite structure of the bulk-phase oxide characteristic of amorphous SiO_2 (region IV). This phase transition is characterised by an intensification of the $p_\pi d_\pi$ interaction and therefore extends up to 30 Å.

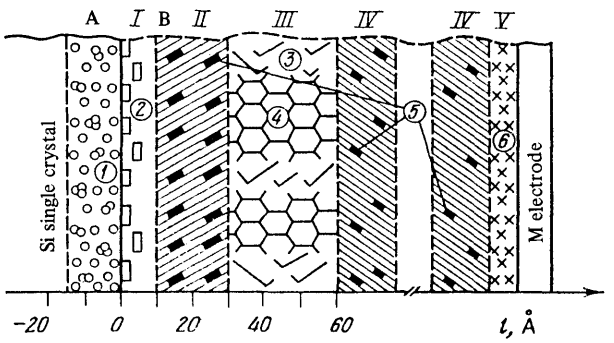


Figure 1. Schematic illustration of the MOS structure on silicon with thermal oxide[19–21,32,33,35]: region A—stretching stresses relaxation zone in a silicon single crystal saturated with interstitial oxygen atoms and clusters (1); region I—transition region corresponding to the non-stoichiometric oxide SiO_x (with $x < 2$) containing inclusions of polycrystalline SiO_2 (2), concentrated predominantly in the immediate vicinity of the interface; region II—existence of the oxide in the short-range and long-range order pseudocoesite modifications with inclusions of nuclear crystals of the oxide (5); region B = region I + region II—compressive stresses relaxation zone in the amorphous oxide; region III—region of the pseudocoesite—pseudotridymite phase transition with dislocation boundaries (3) and hexagonal channels (4); region IV—characteristic region of the bulk of the oxide existing in the short-range and long-range order pseudotridymite modifications with inclusion of 10–50 Å nuclear crystallites of the oxide (5); region V—region of the oxide near the electrode with an incorporated limited space charge and atoms of the electrode metal (6) (the monomolecular and multimolecular layers of the metal oxide exist on the surface of the sputtered metallic polycrystalline electrode at the metal–amorphous SiO_2 interface).

The concept of the fragmented spatial atomic network in the bulk of amorphous silicon dioxide, formed by a mosaic of self-limited ordered clusters–rings formed by 4, 6, and 8 silicon–oxygen tetrahedra, is being developed[20]. The internal boundaries of regions II and IV constitute a system of hexagonal channels and the coesite–tridymite phase transformation region III leads to the formation of extensive defects–assemblies of dislocations. It is difficult to agree with one of the conclusions of the authors of the above studies[20], namely that the multilayer structure of the thermal SiO_2 film is the main cause of the high degree of perfection of the SiO_2/Si system. This conclusion must be compared with the results of other investigations of the structure of the layer of amorphous SiO_2 on single crystal silicon[19,21] from which follows the necessity to take into account the heterogeneity of the material of the oxide film within the layer, in particular, the formation of nuclear crystallites within the bulk of the film with dimensions amounting to tens of angstroms and of polycrystalline inclusions and local discontinuities near the interface[21].

Thus there is a metastable compensation of various defects in the $SiO_2–Si$ system, which is the reason for the marked dependence of the quality and characteristics of the resulting electronic structures[29,34] on the conditions of their formation. In MOS structures it is necessary to take into account also the characteristics of region V—the zone of the dielectric near the electrode, the properties of the dielectric–metal contacts, and the nature of the metal[26]. The phenomena involving the heterogeneity of amorphous silicon dioxide examined above determine the charge instabilities and fluctuations[10,25,27] and their dependence on external factors: the influence of optical radiation[28], γ-radiation[23,24], the presence of impurities[24], and ion transport[30]. In connection with the foregoing, the claim[18] that the properties of vitreous substances are most clearly related to their structure in terms of "average order" is valid.

The influence of the transition layer between the semiconductor single crystal and the amorphous oxide dielectric, which to a large extent determined the concentration of the interphase and surface states of the single crystal, is manifested more distinctly when one used, instead of silicon dioxide, other oxides in the MOS structures, for example, titanium dioxide. In contrast to silicon dioxide, the titanium dioxide layer cannot be grown thermally on the surface of a silicon single crystal and the usual method of its deposition consists in decomposing organotitanium compounds[8,16,36]. The temperature dependence of the degree of crystallinity of titanium dioxide films on single crystal silicon under sputtering and annealing conditions has been published[36] and a schematic description of the structure of the system has been presented: a TiO_2 film on single crystal silicon at different deposition and annealing temperatures. It was observed that, at any TiO_2 deposition temperature, a multicomponent heterogeneous system is formed in which there is a more or less extensive transition layer, the degree of crystallinity of the film increasing sharply with increase of temperature. At a deposition temperature in excess of 550 °C, three phases coexist in the material of the oxide: amorphous phase, anatase, and rutile, while at the optimum decomposition temperature for organotitanium compounds (725–925 °C [16]), almost completely crystalline titanium dioxide (rutile with anatase inclusions) is produced. Furthermore, under all deposition conditions, a more or less extensive polycrystalline transition layer is present in the single crystal–oxide system.

The increase of the instability of the amorphous state in connection with the formation of polycrystalline structures is possible in many technological processes for the preparation of thin oxide films. For example, in the preparation of two- and multi-layer oxide films of the $SiO_2–Al_2O_3$ type[37], there is a possibility of the formation of polycrystalline silicates, while

the interaction of complex oxides in the formation of protective oxide films obtained by anodising the surfaces of semiconductor crystals of the $A^{III}B^{V}$ and $A^{II}B^{VI}$ type can also lead to the formation of polycrystalline compounds. The most general process for these semiconductors involving the deposition of dielectric coatings is therefore the decomposition of organoelemental, usually organosilicon, compounds or silicon halides and hydrides. Depending on the process conditions and the composition of the gaseous or vapour phase, SiO_2 or silicon oxide nitride (SiON) is formed on the surface of the semiconductor single crystal. A transition layer containing the products of the chemical reactions of the material of the film and the single crystal is formed at the interface. The formation of an interface between GaAs and InP semiconductor single crystals and the amorphous dielectrics SiO_2 and SiON deposited chemically on them from the vapour phase has been described[38]. The properties of the interface and the structure of the insulating layers depend greatly on the process temperature and the chemical nature of the semiconductor single crystal. The general inhomogeneity of the dielectric coating has been noted.

The use of organisolicon polymers in electronic engineering holds out most promise and this is in fact the subject of the present review. On must note that such prospects are based on serious experience gained in the industrial manufacture and applications of organosilicon resins and varnishes[42–46] in electronics and semiconductor instrument making.

III. THE SYNTHESIS AND TECHNOLOGY OF THE PREPARATION OF OLIGO-ORGANOSILASESQUIOXANES

The founder of the chemistry and technology of organosilicon compounds is academician K.A.Andrianov, who began his researches in this field in the 1930's and has consistently developed various fundamental and applied fields of organosilicon chemistry, in particular the chemistry and technology of organosilicon polymers.

This review is devoted to the technology, structure, and properties of oligo- and poly-organosilasesquioxanes (OOSSO and POSSO), i.e. organosilicon compounds with a functionality up to three and above. Subsequently the term "functionality (F)" will be understood as the average functionality of the initial mixture of organochlorosilanes (OCS), corresponding to the number of chlorine atoms bound to the silicon atom and involved in the hydrolytic condensation reaction. Compounds with $F = 2.0$ and, in particular, siloxane rubbers have been described in detail in a monograph by Voronkov and co-workers, which lists 5000 references[50], while the industrial technology and certain applications of polyorganosiloxanes have been described in monographs[51,52] and in another publication[53].

The expression "functionality of the oligomer (polymer)" implies that the compound has been obtained by the hydrolysis of a mixture of OCS having the same functionality.

We shall consider mainly studies which have not been covered by earlier surveys[50–52].

1. Preparation of Oligo-organosilasesquioxanes

The preparation of soluble and fusible OOSSO leads to new possibilities in the technology of electronic instrument making. OOSSO hardened directly on a support have come to be used in specific semiconductor instruments and integrated circuits, where they serve as materials of passivating films, active dielectric layers, protective coatings[54–56], and thermal diffusion masks[57] instead of silicon dioxide, obtained traditionally by oxidising the surface of single crystal silicon or by decomposing organosilanes.

In the periodic synthesis of OOSSO [58,59] there is a great probability of the formation of an infusible and insoluble skeletal polymer—gel, while in the hydrolysis of OCS with large substituents there is less likelihood of such a process[60].

The preparation of general purpose dielectrics requires oligomers without a microgel and with a low carbon content (with small substituents), which are synthesised by the appropriate organisation of the technological process.

The residence time of the OCS in the periodic type of reactor is determined by the sum of the time taken to prepare the reactant charge, the reaction time, and the time taken to remove the product. The residence times in the reactor for the first and last portions of the OCS therefore differ greatly, which leads to a considerable scatter of the molecular weights of the resulting OOSSO and the formation of large amounts of gel. The contact time between OCS and the reaction mass in a continuous operation vat reactor with stirring can also differ greatly for the first portions of the reactant according to Levenspiel[61] and Reikhsfel'd et al.[62] Only two-thirds of the OCS introduced is passed straight through the reactor and its contact time is equal to the time taken to traverse the volume of the reactor; 1–3% of the reactant remains in the reactor in constant circulation. With this organisation of the technological process, it is difficult to avoid gel formation and a considerable scatter of the molecular weights of the resulting oligomer. It has been shown[57] that the use of such an oligomer as the electronic resistor for thermal diffusion masks on a semiconductor support does not lead to optimum results.

Other ways of obtaining oligomers without a microgel and with a narrow molecular weight distribution (MWD) in a periodic reactor are possible. Higher alkyltrichlorosilanes with a number of carbon atoms n_C in the substituent between 6 and 10 have been hydrolysed in concentrated hydrochloric acid at the normal pressure[63]. This results in the formation of comparatively low-molecular-weight substances with a high content of hydroxy-groups and having the general formula $[RSiO(OH)]_n$, where R = C_6H_{13}, C_7H_{15}, C_8H_{17}, or C_9H_{19} and n = 6 or 8; they are readily soluble in benzene, toluene, and ether and on heating are converted into liquid alkylsilasesquioxanes having the general formula $[RSiO_{1.5}]_{6;8}$. Their hydrolysis in the absence of a solvent results in the formation of stable emulsions in this instance. It has been suggested that the hydrolysis of higher OCS be carried out under a pressure of 15–80 atm with 0.165–0.465 mole of water per Si–Cl bond[64]. The hydrolytic reaction proceeds via an intermediate[65]. A method has been proposed[66] for the preparation of the oligomer by the hydrolysis of tetraethoxysilane in ethanol. All these methods, which are of undoubted preparative interest, suffer from many disadvantages from the standpoint of the preparation of high-quality dielectric films and coatings for semiconducting materials because the oligomers obtained have a high ineradicable impurity content.

One of the few instances where the periodic organisation of the technological process does not entail a reduction of quality and involves merely a decrease of the yield of the desired product is the synthesis of octaorganocyclo-octasilasesquioxanes[67], for example, octavinylcyclo-octasilasesquioxane[68] or ethylvinylcyclooctasilasesquioxane[69]. A characteristic feature of these compounds are that they can be isolated from the mixture of reaction products by sublimation in the form of pure substances, undergoing a comparatively far-reaching purification under these conditions.

2. The Preparation of OOSSO with Small Aliphatic and Aromatic Substituents

A general purpose dielectric for electronic engineering must meet fairly rigorous requirements—all its dielectric characteristics (ε, $\tan\delta$, ρ_V, E_{br}, the space charge Q_V, and the surface charge Q_S) must be at least not inferior to those of the pyrolytic silicon dioxide and at the same time must ensure either the possibility of the realisation of new physical principles in electronic instrument making or must have sufficient technological advantages which would justify the expenditure on its development and employment. With the periodic organisation of the process or in a discontinuous action vat reactor, it is impossible to obtain products satisfying the above requirements.

One of the most important methods of terminating the growing chain in three-dimensional polycondensation involves the cyclisation reaction[70]. The cyclisation processes in the hydrolytic condensation of OCS are most influenced by the hydrolysis conditions.

On the basis of the foregoing considerations and a number of investigations[60,70-80], one can formulate the principal requirements to be met by the continuous process involving the hydrolytic condensation and cocondensation of OCS, particularly when the functionality of the mixtures to be hydrolysed is $F \geq 3.0$: (1) no mixing of the reaction products with the initial OCS; (2) a minimal residence time of the reaction products in an acid medium; (3) effective removal of heat from the entire volume of the reactant; (4) the universality of the hydrolytic condensation of various OCS and their mixtures with $4.0 > F \geq 2.0$; (5) simple scaling.

For the given conditions, the above requirements are satisfied to the greatest extent by the technological formulation of the processes put forward and justified by Andrianov et al.[70]

In view of the high lability and instability of silanols (the intermediates in the hydrolysis of OCS), the study of the condensation process is difficult. However, this process can be described qualitatively from the standpoint of the kinetics of homogeneous chemical reactions[81,82].

Since the hydrochloric acid formed in hydrolytic condensation catalyses further condensation reactions of the Si–OH groups, an important task in the organisation of the continuous operation process is the regulation of its overall rate. This is achieved by familiar procedures[83]: by introducing an acceptor into the reaction mixture which binds chemically the hydrogen chloride, by analogy with the continuous procedure for the synthesis of tetrabutoxytitanium[36,83]; with the aid of high dilution (with a high yield of cyclic products)[84]; using monomers with large organic substituents at the silicon atom[63,85]; by the preliminary partial alkoxylation (acylation) of the organotrichlorosilanes, as in the industrial preparation of the KO-928 varnish.

In the course of the subsequent hydrolytic condensation, the partly esterified products[80] behave like bifunctional OCS, since the rate of hydrolysis of the Si–Cl bond is much higher than that of the Si–OR or Si–O–COR bond[86].

The hydrolytic condensation of OCS or OCS systems with a high functionality and a small substituent at the silicon atom, in particular the methyl substituent, is accompanied by the formation of methylsilanols, which are extremely labile and sensitive to changes in the pH of the medium[87].

A straight glass condenser with an internal diameter of 20 mm and 700 mm high can serve as a laboratory model of the reactor for the continuous hydrolysis of lower OCS.[70] Under industrial conditions, for example, in the manufacture of the KO-812 varnish, a tubular reactor with the same diameter and height of the tube is used, which is necessary to maintain the hydrodynamic and heat and mass exchange conditions. Laboratory apparatus for the preparation of a solution of oligo-organosilasesquioxane without a microgel is illustrated in Fig. 2. Solutions of oligomers with functionalities in the range $2.0 \leq F < 4.0$ can be prepared on such apparatus[70], which has been demonstrated in relation to a series of industrial recipes for organosilicon resins and varnishes, for example K-5, K-9, K-81, and KM-9. In the lower part of the reactor there is an atomiser through which a solution of chlorosilane is introduced into the water entering the reactor. The volume flow rate of the components is 2.8 ml s^{-1}, which corresponds to an average flow rate of the reaction mixture in the tube of 30 mm s^{-1}. For a specified kinematic viscosity ν, these conditions determine a Reynolds number $Re \cong 300$. For these values of Re and in the absence of perturbations at the inlet, the flow in circular tubes is laminar, which makes it possible to neglect diffusion as a slower concentration equalising process. For the same reason, the temperature and the flow rate are constant throughout the cross-section.

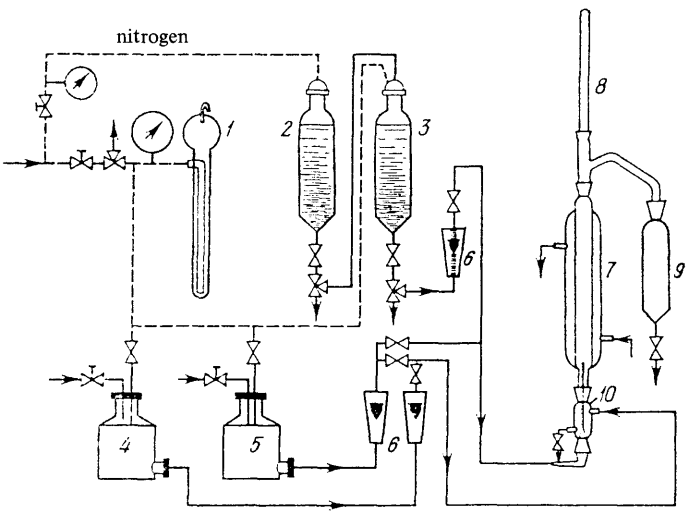


Figure 2. Schematic illustration of the laboratory apparatus for the continuous hydrolysis of organochlorosilanes[73,88]: 1) manostat; 2) reservoir for the preparation of OCS solutions; 3) OCS supply reservoir; 4) water supply reservoir; 5) acetone supply reservoir; 6) flow meters; 7) reactor; 8) thermometer; 9) receiver; 10) partitioning device.

Near the inlet for the OCS solution into the reactor, vigorous turbulent mixing takes place due to the chemical hydrolysis of the OCS, with local evolution of much heat and hydrogen chloride, and also a velocity gradient. The eddy relaxation time τ_V is equal to the ratio of the cross-section of the characteristic volume ($S_p \cong 1$ cm^2) to the viscosity ($\nu \cong 0.01$ cm^2 s^{-1}) and amounts to $\tau_V \cong 100$ s. Comparison of the reaction time $t_r \cong 20$ s and τ_V shows that turbulent mixing of the substance within the limits of the isolated volume takes place throughout the reaction time.

Thus the reaction zone is divided into two sections—the vicinity of the site of injection of the reactants and the rest of the reactor; the hydrolytic condensation reaction of trichloromethylsilane (TCMS) can be regarded as occurring

in two stages: the three-step irreversible hydrolysis of TCMS and the condensation of methylsilanetriol. Since the reaction in the first step proceeds during a very short charactertisic time ($\tau_2 \ll 10^{-2}$ s), one may claim that the entire TCMS hydrolyses during a period shorter than 1 s, which corresponds to the region of the reactor near the nozzle of the atomiser (size ~35 mm), from which the solution of the monomeric methylsilanetriol at a concentration equal to that of the initial TCMS (c_0) enters the reactor.

Methylsilanetriol dimers are formed in the reactor:

$$2H_3CSi(OH)_3 \xrightarrow{k_1} H_3CSi(OH)_2-O-Si(OH)_2CH_3 \quad , \qquad (1)$$

and methylsilanetriol adds to the oligomer:

$$H_3CSi(OH)_2-O-[-Si(CH_3)(OH)-O-]_n-Si(OH)_2CH_3 + \\ + H_3CSi(OH)_3 \xrightarrow{k} H_3CSi(OH)_2-O-[-Si(CH_3)(OH)-O-]_{n+1}-Si(OH)_2CH_3 . \qquad (2)$$

The methylsilanetriol condensation processes are bimolecular, so that the rate of formation of dimers via reaction (1) is defined as $k_1c_1^2$ and the rate of addition of methylsilanetriol via reaction (2) to the oligomer is kc_1c (here c_1 and c are the current concentrations of methylsilanetriol and the oligomer respectively).

The onset of the condensation of silanetriol via reactions (1) and (2) is characterised by the conditions $c \to 0$ and $c_1 \cong c_0$, so that $kc_1c \ll k_1c_1^2$. Hence it follows that the rate of addition must become appreciable only in the final stages of the condensation, but in this case it is also low because by that time virtually no unreacted methylsilanetriol remains in the reaction medium.

In contrast to the studies by Roberts[57] and Pruvost et al.[72], in the investigations of Andrianov and co-workers[70,71,82] reaction conditions ensuring the complete suppression of the gel formation process were rigorously maintained. The formation of the microgel begins when the average length of the siloxane chain ($\bar{L}$) corresponds to ten or more monomer units [$n \geq 8$ in the equation of reaction (2)]. The increase of $\bar{L}$ for all the molecules, for example by a factor of two (due to the condensation of pairs of molecules), is associated with a decrease by a factor of two of the concentration c. Consequently synthesis without the formation of a gel requires that $c \cong 0.1c_1$ during the time $t_r \cong 20$ s. The rate constant $k_1 \cong 1 \times 10^4$ and $K = 1 \times 10^3$ ml mol^{-1} s^{-1}, which depend both on the composition of the reaction medium (the nature and proportions of the solvents, the initial concentration of TCMS, etc.) and on the reaction conditions (temperature, contact time, etc.), satisfy such conditions.

Similar requirements to be met by the process conditions hold also for other OCS with a high functionality—trichlorovinylsilane and trichlorophenylsilane, as well as the products of their cohydrolysis with one another or with TCMS, dichlorodimethylsilane, silicon tetrachloride, and polysilicic acids[71,78,89–112]. The influence of the conditions of the synthesis on the relative contributions of the homofunctional and heterofunctional pathways in the hydrolytic condensation and hence on the composition of the reaction products has been noted in studies of hydrolysis of TCMS [70,71,77,83,113,114] and of the hydrolysis of trichlorovinyl- and trichlorophenylsilanes, the cohydrolysis of various OCS having small substituents, and the cohydrolysis of OCS with silicon tetrachloride and polysilicic acids[78,79,83,87–90,98–106,112]. The generality of the competitive mechanism of the linear chain propagation and cyclic compound formation reactions can be demonstrated in relation to the trimethylsilylation of the inorganic compound $Ag_{10}Si_4O_{13}$, which leads to the cyclisation of the linear chain anion $Si_4O_{13}^{10-}$,[115] by analogy with the hydrolysis of trichlorophenylsilane[99], which leads to the formation of the xonotlitic ribbon [or double chain (Ed. of Translation)] oligomers.

As was to be expected from Eqns.(1) and (2), on decrease of the water:TCMS ratio, the content of the oligomer in the organic phase increases and the losses of the water-soluble products in the aqueous phase diminish. However, when the reaction is carried out when there is a deficiency of water, the scatter of the molecular weights of the products may increase. The methods for the investigation of the hydrodynamic process parameters are applicable to the analysis of the products of the hydrolytic condensation of OCS.[100,101,116]

The kinetics of the hydrolytic condensation of OCS as a whole have been considered[77,81,82,113]; in order to obtain quantitative information about the kinetics of reaction (2), it is apparently useful to employ the kinetic method for the calculation of the MWD of the chains between the branching nodes in non-equilibrium polycondensation reactions[117].

In order to obtain materials with the required characteristics, it is important to know the influence of the conditions and various factors on the formation and structure of the oligomers directly in the technological process[88,90], since the structure ultimately determines, for example, the defectiveness and the film-forming properties of the coatings. It has been stated[79,98,102] that, in the cohydrolysis of trichlorophenyl- and trichlorovinyl-silanes, the resulting mixture does not contain the products of the separate hydrolysis reactions and the fractions of the oligomers and polymers retain the initial ratio of the phenyl and vinyl substituents (3:1).[79]

The hydrolytic condensation of TCMS yields a product which is a complex mixture of polycyclic derivatives with various structures. The synthesis of oligomethylsilasesquioxane in a total displacement flow-type reactor with the parallel injection of reactants in a complex acetone–toluene solvent[118] using the thermostatic attachment has been described[88]. The influence of the synthesis temperature on the physicochemical and electrophysical characteristics of the resulting materials has been investigated. The experimental data indicate an increase of the degree of reaction with increase of temperature (Fig.3).

3. Optimisation of the Continuous Hydrolytic OCS Condensation Process

The hydrolytic reactions of OCS permit the variation of the ratio of the solvents and water within fairly wide limits[70,72,77,78,90,104–106,113]. A significant alteration of the process conditions can change the composition (see, for example, Andrianov et al.[114]) or the structure[89,105] of the hydrolytic condensation products.

The necessity to obtain materials with specified properties brought to the fore the problem of optimisation, whose solution makes it possible to automate the continuous hydrolytic OCS condensation process.

For example OCS systems with $F \geq 3.0$ and a small organic substituent are extremely unstable and tend to form gels. The ratio and the order of introduction of the reaction components, for example, TCMS, acetone, toluene, and water, are important in the hydrolytic condensation of such systems[71,77,83,88].

A definite component ratio for which the process could be carried out without gel formation when acetone is introduced simultaneously with the solution of TCMS in toluene has been found experimentally[70,72]. This ratio has been adopted[118] as a basis in devising an optimisation design. The aim of the optimisation was to reduce the consumption of solvents whilst ensuring the formation of a product free from a gel. In order to minimise the consumption of solvents, a consecutive simplex optimisation method was used, because it is

effective in the solution of problems with several responses and limitations.

Optimisation yielded a point with a minimum consumption of solvents (2.81 litres of solvents per litre of TCMS, which is smaller by a factor of 2.6 compared with the periodic process—by a factor of 2.3 with respect to acetone and by a factor of 3.8 with respect to toluene[118]). Tests[71,88] for the stability of a technological regime without gel formation made it possible to recommend the following amounts of the solvent components per litre of TCMS in the process to be carried out under practical conditions: 2.3 litres of acetone, 0.7 litre of toluene, and 2.3 litres of water (temperature 40° ± 5 °C).

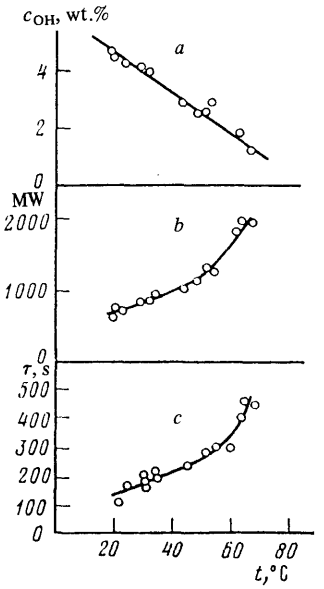


Figure 3. Dependence of the properties of oligomers on the temperature of the synthesis t:[88] *a*) content of hydroxy-groups c_{OH}; *b*) average molecular weight $\overline{MW}$; *c*) gel formation time τ at 200 °C.

The concentration of the required products in the extract and the refined material (in the case of the hydrolytic OCS condensation in the organic and aqueous stages respectively) and the degree of extraction of the reaction products are extremely important technological characteristics of the combined processes involving both chemical interaction and extraction.

The characteristics of the influence of the parameters of the continuous synthesis of OOSSO in a flow type reactor on the concentration of oligomers in the organic and aqueous phases, the content of the hydroxy-groups in the oligomer, the gel formation time, and other characteristics of the hydrolytic condensation products have been investigated[71,77,83,88,113,118].

In conformity with the adopted aim, the concentration of the oligomer in the organic phase, determined from the content of the dry residue, was adopted as the response function and the process temperature, the specific consumptions of acetone, toluene, and water, and the overall volume rate of injection of the components into the reactor were adopted as the factors to be investigated[88,118]. The regression and variance analyses of the resulting equation and its coefficients demonstrated the significance of all the factors investigated except the rate of injection of the reactants (within the limits investigated). The specific consumption of acetone has the greatest influence on the content of oligomers in the organic phase[71,118]; as it increases, the concentration of oligomers falls. The increase of the specific consumptions of acetone and water[71,77,113] leads to a proportional diminution, and an increase of the synthesis temperature[88,118], to an increase of the concentration of the oligomers in the organic phase in the range 19–24%. The concentration of oligomers in the organic phase, calculated from the regression equation for the process carried out under the conditions of the minimum consumption of the solvents, agrees with the experimental value within the limits of the error.

The degree of extraction of the reaction products determines to a large extent whether or not the process is economical. An increase of the synthesis temperature entails a corresponding increase of the yield of the polycyclic products sparingly soluble in the aqueous phase[49,92,114] and hence a diminution of their losses. An increase of the consumption of acetone leads to an increase of the solubility of OOSSO in the aqueous acetone phase and to an increase of the losses. An increase of the consumption of water (a decrease of the concentration of HCl) produces a decrease of the rate of condensation and an increase of the fraction of primary hydrolysis products (organosilanetriols), which are readily soluble in water[49,113] and are carried away with the latter. The complex dependence of the degree of extraction of the products on the consumption of toluene is explained by the fact that the extraction of oligomers from the reaction mixture consists mainly in the extraction from the water–acetone fraction into the toluene–acetone fraction. The initial increase of the degree of extraction with increasing consumption of toluene is therefore associated with the decrease of the solubility of the oligomers in the water–acetone fraction depleted in acetone. A further increase of the consumption of toluene, in which the solubility of the oligomers is low[49], leads to a decrease of the solubility of the oligomers in the organic phase and an increase of the losses of the required product owing to its transfer to the aqueous phase.

The method for the optimisation of the technological process involving the hydrolysis of TCMS can be applied in the study of the hydrolytic condensation of other OCS and the cocondensation of their mixture. Continuous hydrolytic condensation processes with the vinyl-, chloromethyl-, and phenyl-substituted trichlorosilanes have been optimised with the aid of the consecutive simplex method[118] and the data obtained by different workers for the hydrolytic condensation of OCS and their mixtures have been compared[49–51,70,71,77,79,83,87,88,90,92,95,104,113,114].

The possibility of continuous processes involving the hydrolytic cocondensation of TCMS with trichlorosilane, silicon tetrachloride, and polysilicic acid has been examined[89,93–95]. It has been established[70], that the formation of fully soluble products is ensured by carrying out the processes in acetone with subsequent extraction of the reaction products.

4. The Shell Model of the Hydrolytic OCS Condensation Process

The hydrolysable systems in a total displacement reactor have been analysed on the basis of the ideas of the kinetics of homogeneous chemical reactions[81,82] in the presence of

acetone, ensuring homogenisation, in the reaction mixture[121]. However, almost all hydrolytic OCS condensation processes realised in industry proceed as a rule under heterogeneous conditions, which requires allowance for diffusion processes in the study of the polycondensation kinetics. As early as 1959, Sokolov was the first to draw attention to this[119] and proposed a model for the hydrolytic condensation of OCS in a heterogeneous system.

In order to attain a free energy minimum, it is believed[120] that the shell of dispersed-phase species can be divided into several layers. The outer hydrophilic layer consists of solvated molecules of oligo-organosiloxanes. The intermediate layer imparts rigidity to the shell of the globule and consists of oligomers with a wide range of molecular weights. This layer grows as a result of the inflow of the OCS hydrolysis products from the inner cavity within the globule. The inner organophilic layer consists of solvated OCS molecules. Hydrolytic processes, which begin within the inner cavity of the globule, are completed in this layer and the condensation processes, completed in the intermediate layer, begin in it.

The probable mechanism of the heterophase hydrolytic polycondensation was examined above. After the formation of the globules, the rate of reaction is determined by the conditions governing the diffusion of the reactants through the interface[120]. As diffusion processes take place, the intraglobular osmotic pressure increases until the rupture of the shell of the globule accompanied by the ejection into the water–acetone matrix of the contents of the inner cavity of the globule and the formation of a new interface. With decreasing concentration of the monomer, the size of the new globule may not then differ appreciably from the initial size, but the rate of reaction within the globules falls. During the passage of the globule through the reactor, the process involving the rupture of its shell may be frequently repeated.

The above model makes it possible to describe the quantitative picture of the process and to explain the difference in the behaviour of the particles of the solid phase of silica gel or hydrated quartz, tending to coalesce[122,123], and the globules described above, whose surface also contains silanol groups, ensuring the possibility of the polycondensation reaction with formation of siloxane linkages. However, the outer hydrophilic surface of the globules constitutes a barrier which prevents the spontaneous coalescence of the particles coming into contact or colliding. The time of contact between the particles, which in the case under consideration is shorter than 25 s while in the studies quoted above[122,123] it amounted to 10–1000 s, has a definite influence on the aggregative stability of the systems. Nevertheless in the case which we have considered there is also a possibility of the coalescence of the globules when certain process parameters are altered (see, for example, Andrianov et al.[89]), which leads to the formation of an insoluble structured polymer and in some cases also to an uncontrollable reaction—the avalanche-like formation of a gel, which completely blocks the reactor.

The hydrolytic condensation process results in the formation of a solution from which the oligomer can be isolated in the solid state. When the process proceeds with formation of multishell globules, the structure of the oligomers as well as the structure of the polymers obtained from them should depend on the process parameters and the oligomer isolation conditions. An X-ray diffraction study of these relations has been carried out.

The results obtained, presented in Fig. 4*a*, demonstrate the influence of the temperature and the composition of the reaction mass on the changes in the supermolecular structures of the oligomers formed. The degree of crystallinity of all the oligomers is slight (it does not exceed 5%). This precludes a quantitative interpretation of the results—only a qualitative treatment is possible. On the basis of the model of the particle and the process mechanism, the insignificant degree of crystallinity of the oligomethylsilasesquioxanes obtained in acetone can be explained by the decisive influence of the rate of diffusion of the reactants through the outer shell of the globule, which favours the formation of low-molecular-weight crystallisable cyclic oligomers of the type of tetrahydroxytetramethylcyclotetrasiloxane (T_4).

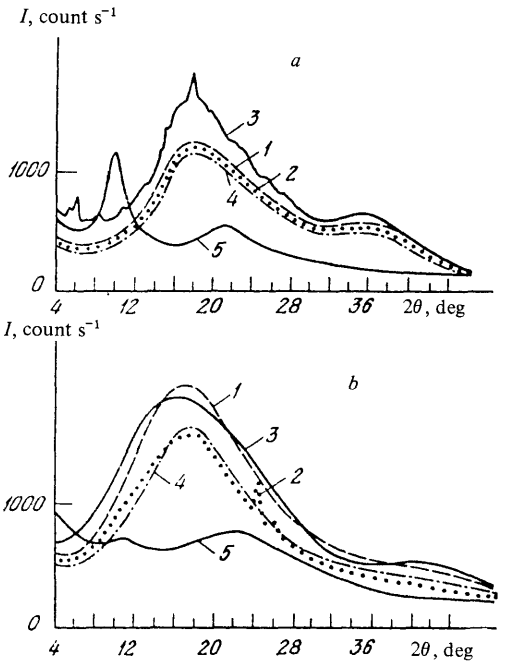


Figure 4. Diffractometer traces for oligo-organosilasesquioxanes (*a*) and polyorganosilasesquioxanes (*b*) (the numbers of the specimens corresponds to those quoted in the Table)[120].

The rate of the subsequent cocondensation of T_4 is reduced as a consequence of the solvation of the hydroxy-groups by acetone. It is significant that the structure of the layer depends on temperature because the constants of the solvation processes and the hydrogen bond formation processes, responsible for the formation of the outer layer, are temperature dependent. When a complex solvent (acetone + toluene) is used, the oligomers formed are amorphous with respect to X-rays.

The data presented in Fig. 4*b* show that the polymers obtained by the condensation of the oligomer containing ~5% of the crystalline phase are fully amorphous, while those obtained by the condensation of the completely amorphous oligomers are apparently crystalline, but the degree of crystallinity does not exceed 5% in this case either.

An additional argument in support of the shell model is the result of the analysis of the width of the first amorphous halo on the diffractometer traces, which is associated with the interchain scattering of X-rays[124,125]. Fig. 4*a* shows the first amorphous halo is extensive (up to $2\theta = 15–18°$), which

indicates an appreciable scatter of the interchain distances, approaching in certain cases 100 Å. Such distances are impossible even for a helical arrangement of the cyclic three-dimensional macromolecules. This indicates the presence of supermolecular formations organised in a more complex manner. The Table lists the half-widths of the amorphous halos calculated from the experimental data (Fig. 4) for the test specimens and, for comparison, the specimen obtained in the presence of a large excess of acetone and water relative to the calculated optimum amount[118]. The Table shows that, while the position of the maximum of the first amorphous halo is relatively constant for all the specimens, its half-width is appreciably altered for the test specimens and is almost an order of magnitude greater than for the control specimen[120].

Dependence of the half-width of the first amorphous halo ($\Delta\theta$) on diffractometer traces for oligomethylsilasesquioxanes on the conditions of synthesis[120].

No. of specimen	T, K	Solvent	$\Delta\theta_1$, deg
1	276	acetone	0.113
2	283	acetone + toluene	0.104
3	280	acetone	0.126
4	278	acetone	0.096
5	313	acetone + toluene*	0.027

*The dilution conditions differ from the optimum conditions calculated by Andrianov et al.[118]

5. Optimisation of the Continuous Process Involving the Synthesis of OOSSO on the Basis of Their Molecular Weight Distribution

In many instances, for example, during the preparation of blended composites, in which it is necessary to ensure an effective distribution of the binder on the filler surface, a wide molecular weight distribution (MWD) is a positive characteristic of the oligomer obtained. Low-molecular-weight reactive cyclic compounds of the type of T_4 or the dimer hexaorganotetrahydroxybicyclotetrasiloxane (T_6) can ensure an even more complete adaptation of the binder as a result of the building up of the oligomeric molecules via a mechanism similar to that of the reactions of siloxanediols with diorganodichlorosilanes[126] or of organocyclosiloxanes with organosilicon diols[127].

However, the attempts to obtain thin dielectric layers and films of polyorganosilasesquioxanes (POSSO) by the polycondensation of the corresponding oligomers lead to negative results in the case of materials with a wide MWD, namely numerous cavities and cracks appear in the film[128], in contrast to the coating obtained on the basis of an oligomer with a narrow MWD.[120]

In order to obtain defect-free structures, one can use one of three methods: the deposition of the polymer or polymerisation on the surface to be protected[11,129-132]; gas and liquid transport chemical reactions and molecular growth ensuring the formation of extremely perfect amorphous oxide films[133-139] (these methods are relatively unsuitable for the formation of polymeric coatings); finally, the preparation of oligomers with a very narrow molecular weight distribution[75, 140] followed by their hardening on the support[109-111].

It follows from the studies devoted to periodic and continuous hydrolytic OCS condensation processes, which dealt with the reaction kinetics[75,81-83,87,88,92-95,104,113,114,141,142] and the MWD of the products formed[49,50,71,75,78,79,88,104,106,120,140], that the formation of products with a narrow MWD can be achieved by altering the conditions in the second stage of the reaction to ensure the predominance of the cyclisation reactions by optimising the process with respect to the MWD of cyclolinear products. The oligomeric intermediates obtained have specific applications depending on the technology of their subsequent converison into the polymer[108-111,140]. The possibility of using cyclic products[71] virtually free of hydroxy-groups as film-forming materials has been demonstrated in studies on the volatility of octaorganocyclo-octasilasesquioxanes (T_8) [69,143] and their polycondensation under the influence of radiation[57,111,140] or catalysts[144-148]. However, despite the comparatively satisfactory characteristics of the films and coatings formed, organocyclosiloxanes with $F \geq 3.0$, in contrast to cyclic compounds with $F = 2.0$,[50] have nowadays found only limited applications[58] in view of the complexity of the technological formulation of the deposition and polycondensation processes, although in the future one may expect their extensive employment in electronics and instrument making as development of apparatus becomes cheaper.

The method of preparation of polymeric dielectric layers from soluble cyclolinear OOSSO, containing 2–4 mole % of hydroxy-groups and with a molecular weight scatter less than 25% is significantly simpler[89,140]. It involves the deposition of solutions of the oligomers on a support by dipping, pouring, pulverisation, or centrifugation with subsequent drying and polymerisation of the material of the film by any of the known methods[52,120,140].

The polymerisation of such oligomers involves preferentially the functional groups and leads to highly cross-linked POSSO [89,140] (as in the study of Katz and Zewi[149]) to which one can apply the statistical model of the structure of a network polymer developed by Topolkaraev et al.[150] for the description of the interrelation between the chemical structure of the initial monomers or oligomers, the kinetics of the condensation reaction, and the technology of the preparation of the network monomer.

In order to obtain oligomers with such characteristics, Kamaritskii[71] used a procedure for the optimisation of the hydrolytic condensation of OCS and in particular TCMS on the basis of the MWD parameters, used as the response, analogously to the procedure described earlier. It has been shown[140] that, when the process is carried out in the vicinity of the new optimum and with a rigorous temperature control in a total displacement flow reactor, it is possible to obtain OMSSO with an average molecular weight $\bar{M} \cong 700$ (with a scatter $\Delta M/\bar{M} \leq 25\%$) and with a hydroxy-group content $c_{OH} = 2$–4 mole %. The products obtained[140] can be described by the revised molecular formula $[H_3CSiO_{1.5}]_{8\pm1.5} \cdot [H_3CSiO(OH)_{1.5\pm0.5}$. The processes involving the subsequent conversion of the OMSSO into the polymer depend decisively on $\Delta M/\bar{M}$ and c_{OH}. The above optimisation has been refined[75] on the basis of the consumption of the raw material components and their ratio taking into account the kinetics of the hydrolytic condensation reaction and, in another study[88], also on the basis of the temperature regime in the process.

6. The Synthesis of Higher-Purity OOSSO; The Possibilities of the Secondary Purification of Oligomers

The dielectrics used in electronic instrument making must meet high requirements as regards homogeneity and purity[151, 152]. The task of improving the materials involves the

improvement of these characteristics or the reduction of the harmful influence of the inhomogeneities or impurities. An example of the reduction of the breakdown characteristics and of the deepening of the breakdown channel, caused by various inhomogeneities in the materials of the dielectrics, has been presented[153].

Polyorganosilasesquioxanes are compounds which are related, on the one hand, to silicates with large cations, forming ribbon structures of the montmorillonite, xonotlite, and kaolinite type[99] (in this sense they fit within the framework of Belov's general classification of silicates[154,155]), and, on the other hand, to silicon dioxide. The properties of silicates and silicon dioxide have so far been investigated in greater detail than those of POSSO, so that the influence of impurities in POSSO can be estimated from their effect on the properties of silicate-based materials which have been studied in detail.

In the industrial manufacture of the KO-812 varnish as well as other organosilicon varnishes[51] and also in the usual laboratory practice, the stabilisation of oligomers in solution is achieved by washing the hydrolytic reaction mixture with a concentrated solution of a salt followed by treatment with KIL clay. The most frequently encountered impurity in POSSO therefore consists of alkali metal ions which are the limiting impurities for silicon and germanium devices and integrated circuits. The Poole–Frenkel' effect has been considered[156] in weak (up to 4×10^5 V cm^{-1}) fields in amorphous silicon dioxide ($E_{br}^{POSSO} \cong 5 \times 10^6$ V cm^{-1}). For films without the limiting impurities, a relation has been obtained between the current density and the applied potential, which has the form usual for the Poole–Frenkel' effect:

$$I = A \cdot \exp\{-(E_{act} - \beta F)^{1/2}/kT\},$$

where the activation energy $E_{act} = 0.2$–1.0 eV, $T = 295$–362 K, and the current density in the oligomers obtained directly by the reaction becomes proportional to n_{Na^+} when the content of sodium ions is only $n_{Na^+} = 10^{17}$–10^{20} cm^{-3}, which is significantly lower than the overall concentration of alkali metal ions (ΣC_M). In oligomers purified to the maximum extent, $n_{Na^+} = 5 \times 10^{13}$–$1 \times 10^{19}$ cm^{-3} and ion transport therefore is unavoidable in MDS structures to which a potential has been applied.

In silica structures there are two types of organisation of the $[SiO_2]_\infty^0$ and $[Si_6O_{17}]^{10-}$ cells—in the form of an infinite three-dimensional network and ribbons of the xonotlite type[157]. The silicates $Ag_{10}[Si_4O_{13}]$ [115] and $[Cu(NH_2CH_2CH_2.NH_2)_2]_4Si_8O_{20}.38H_2O$, incorporating the $Si_8O_{20}^{8-}$ structural element[158] (Fig. 5), are similar or analogous to the silicon–oxygen skeleton of the T_8 – $R_8[SiO_{1.5}]_8$ cyclosilasesquioxane (Fig. 6).[159] This indicates the similarity of the structural elements of amorphous silica, POSSO, and silicates with large cations and, whereas the possibility of a ribbon–ring transition has been demonstrated[115] for the $[Si_4O_{13}]^{10-}$ anion, in other investigations[49,53] the possibility of the reverse ring–ribbon transition, leading to the formation of a large number of terminal $\equiv$Si–O linkages, at which the alkali metal ions are fixed, has been indicated. The increase of the relative number of non-bridging oxygen atoms[160] and ionogenic terminal groups associated with this factor makes possible both ion and charge transport. These results are important for the estimation of the dependence of the dielectric characteristics of POSSO on the degree of their purification, which follows, for example, from the study of Saratov et al.[161]

The influence of the degree of purification of silicon dioxide on the heats of desorption of the dehydroxylation and de-ethoxylation products has been demonstrated[162,163] and in another investigation[164] the dependence of the activity of silica fillers on the chemical composition has been established, which, as will be shown below, has a significant influence on the character of the reaction at the interface[108].

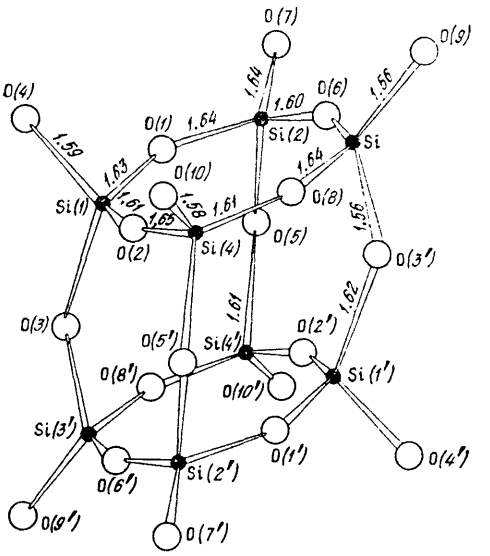


Figure 5. The structure of the skeletal anion $[(SiO_{1.5})_8O_8]^{8-}$.[158]

The sensitivity with respect to active impurities of POSSO with $F \geq 3.0$, having a structure closest to that of SiO_2, and skeletal and ribbon silicates has been investigated[165] by pulsed polarisation and EPR. It has been shown that even very small amounts ($< 2 \times 10^{-2}$ wt.%) of organic free radicals have an appreciable influence on the electret charge and on the character of the EPR spectrum. The statement that there is a possibility of a low-temperature mechanochemical formation of free-radical states in polyorganosiloxanes is of particular interest in this connection[166]. The relaxation of stresses in the large helix of cyclolinear POSSO [121,140] can occur as a result of the rupture of a certain number of $\equiv$Si–O–Si$\equiv$ linkages[89] with formation of ionic[160] and free-radical states[166], which determine the intrinsic impurity content of the POSSO and to a large extent their electret capacity[165]. Inioc states are as a rule to a greater or smaller extent compensated either by external impurities or as a result of the interaction with traces of water:

$$\equiv Si^{\oplus} \quad \quad \overset{O-H}{\underset{H}{|}}$$
$$\equiv Si-O^{\ominus} + \quad \rightleftharpoons \quad 2(\equiv Si-OH)\,.$$

Yet another cause of the formation of inhomogeneities in the structure of oligo- and poly-organosiloxanes may be hydrolytic OCS condensation side reactions due to the presence of impurities in the initial monomers. Admixtures of trichlorosilane can initiate gel formation under the conditions of the hydrolytic condensation of trichloromethyl- or trichlorophenyl-silane, whereas traces of chlorotrimethylsilane induce the effective termination of chain propagation, which is the reason for the necessity for the careful control of the quality of the monomers. A chromato-atomic absorption method for the determination of the above impurities in silicon tetrachloride has been proposed[167].

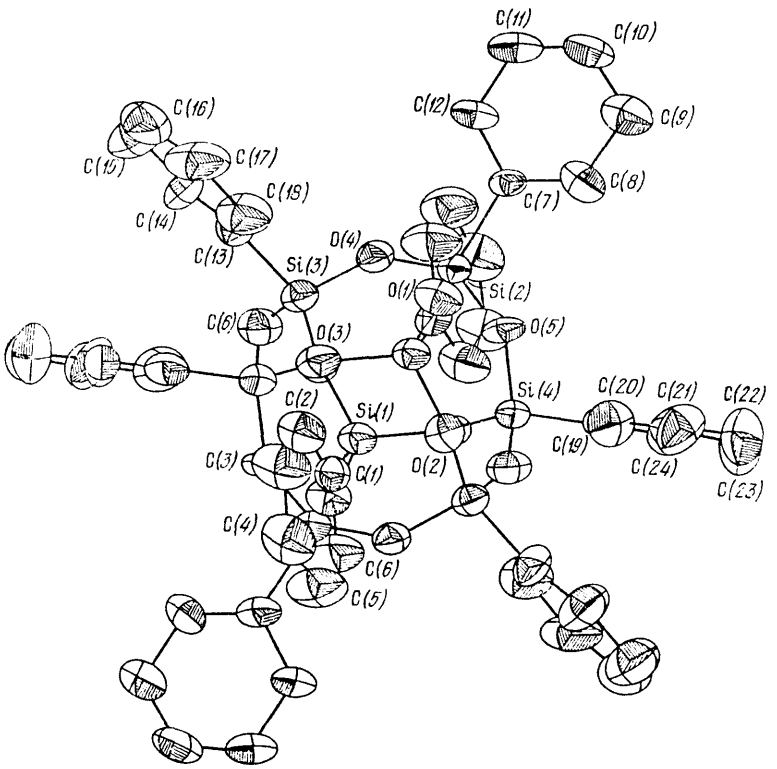


Figure 6. The structure of octaphenylcyclo-octasilasesquioxane $[RSiO_{1.5}]_8$ [projection along the Si(1)—midpoint of the Si(1')Si(2')Si(3')Si(4') face line]. Only the independent atoms have been numbered; Si(1') denotes the atom linked to the Si(1) centre of symmetry[159].

Thus, in order to obtain a sufficiently pure product, meeting the requirements of electronic instrument making, it is essential that the reagents, including the solvents and water, be prepared carefully and also that suitable materials be selected for the technological equipment. Additional purification of the oligomer can be achieved by its reprecipitation from an appropriate solvent. However, it is difficult to hope for sufficiently complete elimination of alkali metal ions from the oligomer, since the ions apparently block some of the hydroxy-groups via ion-exchange reactions of the type

$$\equiv Si{-}OH + Na^{\oplus} \rightleftarrows \equiv Si{-}ONa + H^{\oplus}.$$

The above problem must therefore be solved also by other methods, for example, by limiting the mobility of ions by binding them in complexes with the matrix elements. It is known that for silicon dioxide this aim is attained by doping it with Al^{3+}, which results in the formation of capture centres. The energy characteristics of such centres, namely E_M = 0.50 ± 0.05 eV and H_H = 0.65 ± 0.09 eV, and their content (~1×10^{18} cm^{-3}) have been determined[168]. These data can serve as an approximate guide in selecting the lower limit of the content of the analogous centres in polyorganoaluminosilasesquioxanes, where the aluminium heteroatom has been introduced chemically into the siloxane chain[169].

7. Modification of OOSSO

Careful examination of the technology of the preparation and purification of OOSSO to make possible their use as dielectric materials in semiconductor electronics[108–111] led to the discovery of the special role of the phenomena on the surface of the support and in the immediate vicinity of the interface[108,170] of the solid phases, of the special significance of the presence and concentration of hydroxy-groups, traces of water, and limiting impurities, of the structure of the amorphous phase (in particular the ratio of the short-range and long-range disorders), and of the stresses arising both in the bulk of the amorphous films and at the interface with the support and in the support itself. Studies of amorphous and crystalline silicon dioxide proved productive for the elucidation of these problems. Studies of very thin films[171,172], both natural (grown by oxidising the surface of silicon) and deposited in a high-frequency discharge plasma, have in general not altered but merely refined the details of the picture of the boundary region illustrated in Fig. 1. One can actually state that silicon dioxide films with an increased content of carbonaceous impurities[173] and hydroxy-groups[17,174] or films formed under the decisive influence of water vapour[17,175] have come to be more vigorously

investigated during the last decade. This trend is associated with the fact that the presence of a limited amount of impurities, which do not greatly diminish the dielectric characteristics of the amorphous oxide, makes it possible to compensate for the disadvantages of SiO_2 discussed above. In this connection, investigations of the state of the OH groups in quartz[176] and silica[177], of the collective states for different modifications of SiO_2,[178–181] and of the structural defects in amorphous SiO_2 films on the surface of single crystal silicon[182] have developed greatly.

An important addition to all that has been said before about the SiO_2–Si reference system involves allowance for the stresses arising in multilayer structures. For example, a study has been made[183] of the influence of heat teatment on the stresses in amorphous silicon dioxide films deposited on a support by electron beam evaporation and a fairly old study[184] provided a general method for the estimation of internal stresses arising in multilayer structures. However, the study of the influence of the doping process on the relaxation processes in silicon dioxide layers is of greatest interest from the standpoint of the usefulness of the modification of siloxanes[185].

Silicon dioxide meets the principal requirements of electronics and electronic instrument making and is technologically convenient but is diffucult to modify. A material capable of competing with amorphous silicon dioxide should have effective dielectric properties, should be no less technologically convenient, and should be readily modified. These requirements are satisfied by structures based on POSSO.

(a) Modification of OOSSO by the introduction of a heteroatom directly into the siloxane chain. The modification of OOSSO by the introduction of Al, Ti, and Pb atoms into the siloxane chain in order to obtain polyorganoelementosiloxanes with improved dielectric characteristics different from those of POSSO has been described[111,128,169]. Aluminium heteroatoms were introduced in order to reduce the mobility of the alkali metal ions (mainly sodium ions), titanium atoms were introduced to increase the dielectric constant of the material, and lead atoms were introduced to reduce its permeability to accelerated ions[111]. The most important condition governing the modification was the retention of the non-crystallisability of the material over the entire range of its operating conditions (this was first observed for unmodified POSSO [89]).

There exist a series of methods for the introduction of the aluminium heteroatom into the siloxane chain. The preparation of oligomeric alumino-organosiloxanes by the reaction of aluminium compounds (for example, aluminium isopropoxide) with α,ω-dihydroxyorganosiloxanes having the general formula HO[RR'SiO]OH, where R = methyl and R' = methyl or vinyl, formed via a reaction, involving the opening of the ring in the corresponding organocyclosiloxanes with an alcoholic solution of alkali[128] followed by the neutralisation of the products with acetic acid, is technologically the most convenient. Depending on the reactant ratio and the nature of the siloxane diols employed, different oligo-organoaluminosiloxanes have been synthesised: oligodimethylaluminosiloxanes with the silicon : aluminium ratios g = 4, 8, and 12; oligomethylphenylaluminosiloxanes with g = 1.8, 2,4, 3.6, 4.25, and 13.2; oligomethylvinylaluminosiloxane with g = 12. The reaction scheme, for example, in the case of an equimolar reactant ratio, is

$$Al(OC_3H_7)_3 + HO-[-SiRR'-O-]_n-H \rightarrow -\underset{\displaystyle OC_3H_7}{\overset{|}{Al}}-[-OSiRR'-]_n-O- \ .$$

Linear oligomers are formed, which is confirmed by the presence of an infrared band with $\bar{\nu}$ = 1130 cm^{-1}, caused by the vibrations of the C–O bond in the isopropyl group. With increase of the relative amount of siloxanediol, i.e. in the presence of an excess of Si–OH groups, this band disappears, which is associated with the formation of network oligomers. It is significant that oligomers without hydroxy-groups are formed in this case, which follows from the absence of the characteristic infrared absorption bands in the range 3200–3600 cm^{-1}.

Consequently in the aluminium isopropoxide–siloxanediol system there is a possibility not only of heterofunctional cocondensation but also homofunctional cocondensation of siloxanediols, catalysed by aluminium compounds, takes place. The oligomers formed are readily soluble in organic solvents.

Films of oligo-organoaluminosiloxanes (OOASO) have been obtained[128] from toluene solutions on glass, silicon, and steel supports. The polymerisation was carried out by heat treatment and was accompanied by the loss of fusibility and solubility of the films. The rigidity of polyorganoaluminosiloxane films increases with decrease of the ratio g.

Satisfactory coatings are obtained on the basis of MM-12, MV-12, and MF-13.2 varnishes.

A stronger intermolecular interaction in polyorganoaluminosiloxanes compared with POSSO has been established[128] and has been confirmed by infrared spectroscopic data. It is associated with the presence of the aluminium atom in the siloxane chain. The dielectric parameters of polyorganoaluminosiloxanes satisfy the requirement that their functionality be high while retaining the non-crystallisability characteristic of OOSSO. In addition, polyorganoaluminosiloxanes are characterised by the reduced mobility of alkali metal ions compared with POSSO and SiO_2, which makes it possible to reduce appreciably the time drift of the parameters of silicon semiconductor devices.

The method of preparation of modified OOSSO by the synthesis of spiro-compounds, whose range is apparently largely limited to compounds of Group IV elements, for example, titanium-containing compounds, is promising[186].

In principle, there is a possibility of other procedures for the synthesis of oligo-organoelementosiloxanes: the synthesis of reactive monomers incorporating a heteroatom[109–111,187,188] and the interaction of OCS with the oxides and hydroxides of elements under special conditions (for example, a study has been made[189] of the interaction of TCMS with titanium dioxide in a fluidised bed). However, such processes are less selective than the specific synthesis of oligomers with a heteroatom in the siloxane chain and can lead to oligomers incorporating a heteroatom both directly in the siloxane chain and in the surrounding groups.

(b) Modification of OOSSO by the introduction of a heteroatom into the groups surrounding the siloxane chain. Numerous studies surveyed in monographs[48–50,52,92,190] and others[83,96,191,192] were devoted to the influence of the groups surrounding the siloxane chain on the properties of polyorganosiloxanes (POSO). The vast majority of such investigations involve the replacement of the alkyl group by an aryl or alkoxy-group. Such modifications of the surrounding groups are undesirable, since they involve an increase in the relative content of carbon which constitutes a limiting impurity in the dielectric–single crystal silicon (germanium) structures, which one attempts to avoid as far as possible in the formation of metal oxide films and coatings[16].

More homogeneous materials with a better distribution of modifying heteroatoms can be obtained by opening three-dimensional cyclic structures of the type of T_8, T_{10}, or T_{12} with formation of compounds having a ladder (double stranded)

structure[53] with the simultaneous introduction of organometallic compounds, tetrabutoxytitanium[36,83], tetraethoxysilane, etc.[165,193], which add to the non-bridging oxygen atoms. The influence of the metal on the siloxane chain via an oxygen atom is localised in mono- and oligo-elementosiloxanes in the vicinity of the M–O–Si group[161]. The oligomers formed in this way retain their capacity for polymerisation and the corresponding polymers, while possessing the specified dielectric characteristics, retain their non-crystallisability characteristic of POSSO.

(c) Modification of POSO by chemical doping. The method of chemical doping makes it possible to alter sharply the characteristics of polymers using comparatively small amounts of dopants and additives, imparting to such polymers and the materials based on them special properties necessary for specific applications[194,195]. It is know that in the thermal and thermo-oxidative stabilities of polydiorganosiloxanes increase appreciably after the introduction of a series of heteroatoms into the main chain[50,196]. A similar effect can be achieved also by the introduction into the polymer matrix of certain low-molecular-weight siloxanes[197] or elementocyclosilazanes (for example, those containing the titanophosphinate group), whose effect apparently consists in the formation of rare interchain cross-links. Even when their concentration is very low, such cross-links alter the properties of the polymer, which can no longer be regarded as linear; its thermal stability, mechanical properties[198], and electrical strength are changed.

When the POSSO has already been formed, this mechanism cannot operate and chemical doping is carried out in the stage involving the formation of an oligomer film by introducing small amounts of organometallic or organic compounds which react with the oligomers and are incorporated in the polymer matrix in the course of hardening[165,193]. This method makes it possible to control within certain limits the electrophysical and particularly the electret characteristics of the materials. In this case, apart from the formation of additional cross-links between the elements of the helix or between the cyclolinear chains of the polymer, the additives can be incorporated into the groups surrounding the main chain. The relative contributions of these processes are determined both by the conditions governing the introduction of the additives and by the conditions in the hardening of the polymer.

As in the doping of semiconductors[3], the POSSO chemical doping processes involve a fundamental difficulty associated with the limited capacity of the matrix, i.e. the fact that it can incorporate in its structure not more than a strictly specified amount of the dopant. Beyond these limits, phenomena, which as a rule vitiate all the advantages achieved by the modification of the initial matrix, take place. It is difficult to say what constitutes the starting point of the impairment of the material: the appearance of presegregations of a new phase or the breakdown of the sections of the matrix adjoining directly the regions of the support with an electric field gradient (surface defects, charged impurities, outcrops of dislocations on the single crystal surface)—it is difficult to separate these two processes in time. This is followed by the appearance of discontinuities in the matrix with segregation of the impurity along the boundaries of the macroblocks, analogous to those described by Spektor[199], and finally crystalline or amorphous inclusions of the independent phase of the dopant or the products of its reaction independent of the matrix are formed. Under the conditions of doping at concentrations far outside the limits of the chemical capacity of the matrix, all these effects operate simultaneously[193].

The modification procedures enumerated above, in particular chemical doping, depend greatly on the conditions governing the conversion of the OOSSO into the corresponding polymers and also on the chemical nature of the oligomers and modifying agents employed.

IV. OLIGOMER POLYCONDENSATION PROCESSES

In view of their instability (tendency towards structure formation in both the solid state and in solution)†, oligoorganosilasesquioxanes are of no practical value.

In order to convert these intermediates into the finished materials, it is necessary to convert the oligomers into the corresponding high-molecular-weight products. The general characteristics of the polycondensation of OOSSO have been examined in a number of studies[49,50,52,53,78,89,90,92,119,129,275]. In the heat treatment of oligomers, one can arbitrarily distinguish two stages of the process. The first stage develops in the oligomer melt at temperatures in the range 70–120 °C [depending on the molecular weight (M_{OOSSO}) and on the MWD of the oligomer]. The second stage takes place in the solid phase after hardening. Competing reactions are polycondensation involving hydroxy-groups and ring opening. In fact the temperature ranges of these reactions overlap to only a slight extent—the first reaction is almost completed after the attainment of 200 °C, while the second reaction is only beginning at these temperatures. However, both reactions influence the formation of the structure of the POSSO matrix. Taking into account the data on the structure of amorphous silica[157], it is necessary to postulate the presence of residual hydroxy-groups in POSSO up to temperatures exceeding significantly that of the thermal or thermo-oxidative elimination of hydrocarbon groups[120]. The presence of residual hydroxy-groups in the POSSO matrix plays an important role in the interaction of POSSO with the supports[108]. Low-molecular-weight compounds of the type of T_8 and other three-dimensional cyclic compounds undergo thermal polymerisation with difficulty. Catalytic reactions with ring opening[53] of the type of the polymerisation of cyclic oligomers with $F = 2.0$ [145,147,201] or cross-linking under the influence of high-energy radiations[57,110,111], are more characteristic of these compounds.

The process which is more likely to take place in the solid phase under the influence of high temperatures[202] involves the elimination of organic groups, which leads to the formation of a material whose properties are similar to those of silicon dioxide[120]. However, the purity of this material, obtained under the usual conditions in bulk, is greatly inferior to that of silicon dioxide obtained by fusing quartz, by the oxidation of the surface of silicon, and even by the decomposition of tetraethoxysilane or other organosilicon monomers. This is associated with the fact that the thermal degradation of polyorganosiloxane, like that of polyorganoelementosiloxanes[203], entails the segregation of a new phase in the form of a cluster or colloidal carbon or of graphite inclusions accompanied by the darkening of the material. High-energy radiations (ultraviolet radiation, X-rays, and neutron, electron, and proton beams) have an effect similar to high temperatures as regards the degradation of the polymers.

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†An exception to this rule is provided by cyclic three-dimensional compounds, for example, octaorganocyclo-octasilasesquioxanes, which form an independent subclass of silasesquioxanes[200], but these also have poor mechanical properties.

The influence of ultraviolet radiation in the region of 265 and 420 nm and of proton beams with an energy of 500 keV on POSSO has been investigated[204,205] as a function of the organic group and it was shown in particular, that the replacement of 27–50 mole % of the methyl groups in PMSSO by phenyl groups increases appreciably the radiation stability of the polymers. The resistance of the organic groups, particularly phenyl groups, to the action of temperature and irradiation can be significantly increased by introducing into the organosiloxane matrix transition metals or other complex-forming fillers[206–209].

The preparation from POSSO of a material whose composition is identical to that of silicon dioxide, which is essential for applications in electronics, becomes possible in the thermo-oxidative annealing of thin (up to 1 μm) PMSSO films with $F \geq 3.0$.[120] In this case the process *in vacuo* can be described by the overall equation

$$\{H_3CSiO_{1.5}\}_n + 3n/2\,O_2 \rightarrow \{SiO_2\}_n + nCO + 3n/2\,H_2O\ .$$

Volatile reaction products leave the film without causing breaks in its continuity. The process leads to the formation of new siloxane linkages, giving rise to interchain cross-links.

In studying the temperature dependence of the polycondensation mechanism, one must take into account the fact that, as shown, in particular, in the study of Andrianov et al.[108], the heterolytic mechanism of the cleavage of siloxane linkages predominates at moderate temperatures (up to ~400 °C):

$$\equiv Si{-}O{-}Si\equiv \rightleftarrows Si^{\oplus} + \equiv Si{-}O^{\ominus}\ ,$$

while at higher temperatures (above 400 °C), the homolytic mechanism predominates:

$$\equiv Si{-}O{-}Si\equiv \rightleftarrows \equiv\dot{S}i + \equiv Si{-}O^{\cdot}\ .$$

The low-temperature hardening of siloxanes is accelerated by ionic catalysts[144,146,210]. The coexistence of various polycondensation mechanisms can be illustrated by the results of its determination of the rates of hardening of thin oligomer films on various supports (Fig.7).

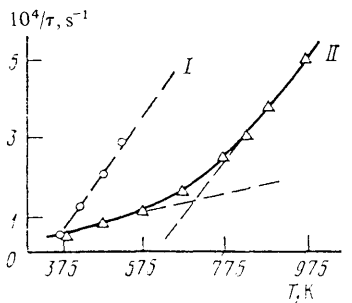


Figure 7. Dependence of the rate of hardening of oligomethylsilasesquioxane on different supports: I) on a metal; II) on single crystal silicon.

The knowledge of only the general characteristics of the polycondensation of OOSSO is insufficient for the development of processes leading to the formation of dielectric films and coatings directly on the surfaces of any semiconductors.

For a better understanding of the problems arising in the development of such materials, we shall list the main requirements which they must meet:

(1) Dielectric properties not inferior to those of amorphous silicon dioxide ($\varepsilon \cong 3.0$; $\tan\delta \cong 1 \times 10^{-2}$; the number $n_{por} < 5\ cm^{-2}$; $E_{br} > 1 \times 10^6\ \Omega\ cm^{-1}$; $\rho_V > 1 \times 10^{14}\ \Omega\ cm$; $Q_V \cong 5 \times 10^{11}$ e.s.u. of charge per cm^2; $\mu_M^{POSSO} \cong \mu_M^{SiO_2}$).

(2) The maximum attainable layer and surface homogeneity in the absence of any inclusions of another phase.

(3) Minimal stresses both in the bulk of the dielectric film and at the interface with the semiconductor.

(4) Maintenance of the concentration of the surface states of the protected semiconductors at the initial level and if possible its reduction.

(5) Resistance to the action of corrosive media (NH_3, PH_3, AsH_3, etc.), moisture, and solvents.

(6) Resistance to the action of accelerated ions.

(7) Capacity for being modified within fairly wide limits at least as regards ε and Q_V ($2.0 < \varepsilon < 15$; $1 \times 10^{10} < Q_V < 1 \times 10^{14}$) with retention of other dielectric characteristics at a fairly high level.

(8) Capacity for being etched with standard solvents at rates v_{etch} comparable to $v_{etch}^{SiO_2}$ and capacity for being modified as regards v_{etch}.

Naturally no one material can meet all these requirements simultaneously. It is necessary to create a series of materials of one class obtained by isotypical technological processes.

Dielectric materials likely to be useful in electronics and instrument making have been developed in a series of studies[36,55–57,70–75,83,86,88,89,99,107–112,118,120,128,140,160,165,169,170,193,194,211,212,275] in conformity with these requirements on the basis of comprehensive investigations of the relation between preparation and conversion conditions and the molecular and phase structure of the products with control of the physicomechnical and electrophysical characteristics.

Homogeneous oligomers free from particles of a heterophase (gel) are obtained in a total displacement flow reactor with parallel injection of the components. A broad MWD complicates the technology of the hardening of the oligomers. Fusion within wide temperature limits results in the existence of the oligomer in the form of a two-phase system throughout some time from the beginning of the process. Reactions in the liquid phase are faster than in the solid phase, so that polymerisation in the melt is completed, while part of the oligomer has still not fused and, by the time when the residual oligomer has melted and begun to polymerise, the head fraction has already solidified. Furthermore, the polymerisation conditions near the upper limits of the fusion temperature range differ from the initial conditions, which creates an additional inhomogeneity and stresses in the films. It has been noted[78,90] that larger oligomeric seeds create a more defective structure.

Under the conditions of a wide MWD, the growth of large helices is hindered, the alternation of helical and xonotlitic structures becomes possible[99] and the presence of such comparatively small ribbon inclusions can reduce the electrical strength of the material. Thus, in order to obtain high-quality dielectric films based on POSSO, it is preferable to have an oligomer with the narrowest possible MWD (in the limit, individual oligomeric molecules) and this dictates the necessity to optimise the synthesis of the OOSSO with respect to the MWD.

In order to obtain the composites and press-materials based on OOSSO, some of the solvent is left in the oligomer as a binder before the final polymerisation stage. This ensures more effective mixing and moulding of articles and also reduces the adhesion of the composites to the press-moulds.

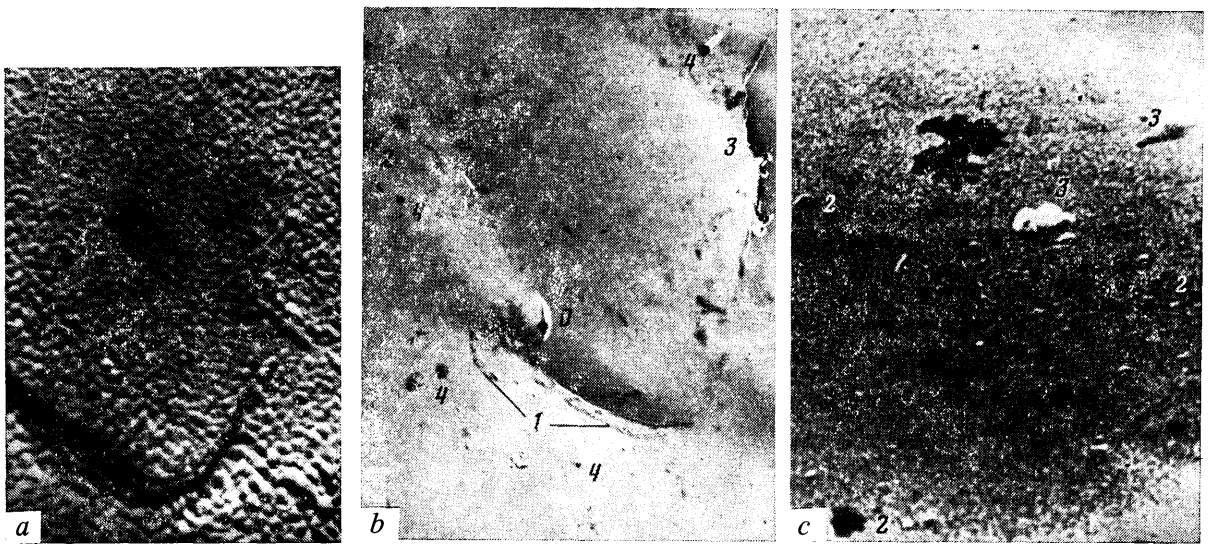


Figure 8. Comparison of the structures of regions of polymethylsilasesquioxane and amorphous silicon dioxide films (×420) which have undergone electrical breakdown[120,140]: *a*) ideal surface of PMSSO film with different thicknesses; *b*) breakdown of the ideal PMSSO film (the Al electrode is deposited on top) on single crystal silicon (10 breakdown steps in one region with restoration of electrical stability after 9 cycles); *O*—centre of breakdown crater; 1) surface fusion of the material of the electrode along the breakdown trajectory; 2) breaks in the Al electrode with surface fusion associated with surface electrical breakdowns; 3) massive breaks in the Al electrode associated with electrical breakdown by reverse currents; 4) satellite punctures in the Al electrode; *c*) electrical breakdown of a film of amorphous silicon dixoide (the Al electrode is deposited on top) on single crystal silicon (single electrical breakdown): 1) breakdown crater; 2) satellite breaks on the periphery; 3) ejected surface-fused material of the electrode.

When thin films are formed over a large area, this method is unsuitable because numerous defects (for example, large and small open and closed bubbles) are formed on the surface of the film in this instance; they are produced when the solvent and the water formed in the polycondensation process are removed. Although such shallow defects do not influence the integral dielectric properties of the moulded POSSO films, they can prove to be weak sections in local electrical breakdown. Hardening is therefore carried out under controlled conditions[120,128,140] ensuring the removal of the solvent and condensation of water through the surface of the film.

The dielectric layers formed in this way and based on polymethylsilasesquioxane, polyphenylsilasesquioxane, and other POSSO [89,108–112,120,140] are distinguished by homogeneity throughout their bulk and an even surface (Fig.8*a*) with average dimensions of the rugosities (of the type of spherical growth formations) smaller than for thermo-oxidative silicon dioxide[213] and with smaller ejections of the dielectric material on repeated electrical breakdown than in the case of a single electrical breakdown of an SiO_2 film (8*b* and 8c).

Unfortunately direct control of the OOSSO polycondensation processes on the protected surfaces is difficult to achieve by traditional methods in view of the small thickness of the films formed. However, bearing in mind the initiating effects of the point defects in a silicon single crystal[108], one can employ the results of the study of these processes on specimens of the free oligomer.

The weight loss effects and thermal phenomena in the polycondensation of a number of oligomers have been investigated[214].

V. PROBLEMS OF THE INTERACTION OF OLIGO- AND POLYORGANOSILASESQUIOXANES WITH A SOLID HETEROPHASE

The first applications of POSSO with high functionality were associated with their thermal stability and hydrophobic properties. Parameters of the materials such as their resistance to high temperatures and ionising radiations[202–205,209] and corrosive media[215–217], mechanical characteristics[198] and low cost achieved by a wide variety of procedures for the preparation of binders[71–73,107,218–222] and composites based on them[223–229] were also of decisive importance at this stage. In this first stage of research, composities with interesting electrophysical[55,152,190] and electronic[229] characteristics were already obtained. Studies involving the investigation of the mechanisms of the interaction of reactive monomers[133,189, 192,230–233] and oligomers[133,233–236] with the solid phase of the filler (textile fibres, silicates and cements, silica gel, and aerosils), taking into account the functionality of the groups on their surfaces[236,237], may be regarded as the next stage. Finally, the general postulates concerning the interaction at the interface between two solid phases, one of which is an organosilicon dielectric, were formulated[108,170] on the systemtic basis of ideas concerning the transition layer in semiconductor–dielectric and metal–dielectric systems[7,8,13,35,36, 238–240] and the structure of the surface layers of amorphous element–oxygen solid phases[160,180,241], as well as experimental data obtained for the organosilicon dielectric–silicon and organosilicon dielectric–metal systems[54,56,109–111,120,128,129,140, 151,165,169,193,212].

1. Blended Compositions Based on Organosilicon Binders

Problems concerning the formation of compositions filled with glass fibre and their characteristics have been described comprehensively in the literature[47–53,92,190], so that in the present section we shall therefore consider only individual examples of blended compositions based on organosilicon binders (OSB) [71,107] which are of interest either as regards their applications or from the standpoint of the general characteristics discovered.

The possibility of employing organosiloxanes in the electrotechnical industry for the formation of insulating layers and enamels having an improved heat resistance, and reduced flammability and with a low evolution of toxic volatile substances was first examined by Schwarz[129]. A number of studies have been devoted to problems of the thermal stability of composites based on filled polyorganosiloxanes[206–209,223,224]. It has been noted that the thermal stability of polyphenylsilasesquioxanes filled with metals increases as a function of the filler metal in the sequence Pb < Fe < Ni < Bi < Cd < Cu < Co. The activity of the metal is determined not only by its chemical nature but also by its degree of dispersion, which has been confirmed in relation to the composite of OSB and iron carbonyl powder[226].

A report[223] describes the creation of a series of thermostable and corrosion-resistant dielectric compositions based on oligomers obtained by the hydrolytic condensation of OCS (TCMS, trichlorophenylsilane, and dichlorodimethylsilane) in the presence of iron(III) chloride and zinc or aluminium dust or titanium dioxide as fillers and the possibility of modifying varnish compositions by means of organic solvents and by adding a polyester (in the case of hot hardening: 2 h at 180–200 °C) or an alkyl resin (in cold hardening; 2 h at room temperature) was examined. Another report[224] is devoted to a comparative study of the characteristics of enamels made from these composites placed on steel supports. For satisfactory dielectric parameters, the best thermal stability is shown by the polymethylphenylsiloxane enamel with zinc dust and the greatest chemical stability and resistance to the atmosphere is shown by an enamel with the rutile titanium dioxide phase modified with 20 wt.% of polyester.

The definite structural similarity between POSSO, particularly those obtained under specific conditions[99], and silicates with large cations[154,155] was already mentioned previously. The study of the interaction and structrual transformations in POSSO composites with iron-containing chrysotile-asbestos[227] and OSB with fluorophlogopite[228] is of definite interest in this connection. The first composition is of special interest, since the supermolecular organisation of chrysotileasbestos, having the formula $Mg_6[Si_4O_{11}].(OH)_6.H_2O$, belongs to an extremely rare type of tubular crystals and agrees well with the helical organisation of POSSO.[140] Furthermore, it can be seen from the formula that this mineral contains a large amount of active hydroxy-groups and, in view of its intrinsic low (mainly ionic) electrical conductivity and capacity for cocondensation via the hydroxy-groups with OOSSO, this ensures a high thermal stability and effective dielectric characteristics of the composite[227].

The most striking result in the application of blended OSB composites with a filler in electronic instrument making has been achieved in the study of photocapacitive characteristics of inhomogeneous structures consisting of dispersions of photoconducting microcrystalline cadmium sulphide particles in an organosilicon varnish[229]. The possibility of developing photovaractor elements for the frequency range 10^3–10^6 Hz for illumination intensities of 10^{-2}–10^3 lm with a maximum overlap coefficient of ~5 has been demonstrated experimentally.

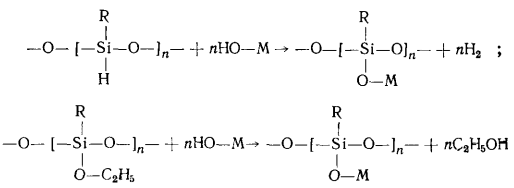
2. Cocondensation of Mono-, Oligo-, and Poly-Organosiloxanes with Functional Groups on the Surface of a Solid Phase

The interface formation processes in the reaction of mono-, oligo-, and poly-organosiloxanes with amorphous or polycrystalline oxide phases are fairly complex. In this case the structure of the phase of the support "dictates" the structure of the junction boundary, as shown in a study[241] in which the author emphasises the decisive role of the short-range order of the formation of the surface layer in the molecular deposition of oxides layer by layer using the principle of the isoenergetic state of oxygen, characterised in any solid stable oxides by the approximately constant overall bond energy $E_{E-O} \cong 240$ kcal g-atom^{-1}. A calculation (tested experimentally) has been carried out by the extended Hückel–Hoffman method specifically for the [SiO_4] tetrahedron in SiO_2 and led to the following results: charge on the oxygen atom $N_O = -0.93$; population (total order) of the Si–O bond $P_{Si-O} = 0.539$; bond energy $E_{Si-O} = 104.3$ kcal mol^{-1}; π-bonding ~16%; coordination number $k = 2$; overall electron population of the oxygen bond in the silicon dioxide lattice $kP_{Si-O} = 1.078$, i.e. $kP_{E-O} \cong 1$ as in other stable oxides. These conclusions are in good agreement with the results of a study[180] where data for the splitting of the optical frequencies in the spectra of amorphous bodies led the authors to the conclusion that the influence of the orientation of the silicon–oxygen tetrahedra makes a small contribution and that account must be taken of the long-range effect by introducing a term related to the Coulombic forces determined by the presence of effective charges on the silicon and oxygen atoms. The state of the hydroxy-groups on the surface of the oxide has been investigated in detail[241] and the cause of the difference between the states of the hydroxy-groups on the surfaces of aerosils and quartz glass with [SiO_4] octahedra, on the one hand, and silica gels and silicic acid hydrogel with [SiO_6] hexahedra, on the other, was discussed. In this case the difference is caused by the binding of the OH group to the nearest silicon atom, whose state also depends on the coordination. The conclusion[241] that there are different states of the OH groups on the SiO_2 surface has been confirmed by the preparation of aerosils with isolated amino-groups on the surfaces[237].

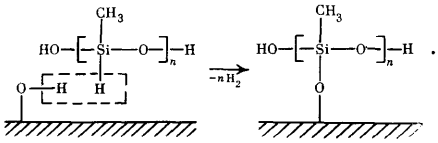
These studies, carried out on simple objects, permit at least a qualitative understanding of the processes occurring on the surfaces of materials related to polyorganosiloxanes[134,233,235,236].

It has been shown that the interaction of polydimethylsiloxane rubbers with aerosils proceeds via the silanol groups[236], which is confirmed by the different behaviour of rubbers with free and blocked terminal silanol groups. However, physical interaction forces nevertheless play a decisive role in the above system, which is manifested by a decrease of the content of the polymer bound to aerosil at temperatures in excess of 200–240 °C. On the other hand, when the surface of highly dispersed silicon dioxide was modified by low-molecular-weight silazanes and siloxanes, the formation of a chemical bond between the surface of silicon dioxide and the compound employed was established[134]. It has been shown[34] that the different interactions of the organosilicon monomer and oligomers[233] with Portland cement having the composition (wt.%) 22.06 SiO_2, 3.98 Fe_2O_3; 3.89 Al_2O_3, 63.9 CaO, 2.68 SO_3, 1.65 MgO, 1.42 H_2O, and 0.27 Na_2O and its fully hydrated (to the extent of 99.9%) modification is determined mainly by the relative contributions of two processes: chemical reaction involving the active groups (Si–H, Si–OH, and Si–OR) and adsorption. The products of the chemical reactions were identified chromatographically[233]. For example, the presence of molecular hydrogen and ethanol in the products is attributed to the occurrence

of the following processes:



The detection of molecular-hydrogen is particularly important, confirming the mechanism proposed by Reikhsfel'd et al.[234]:



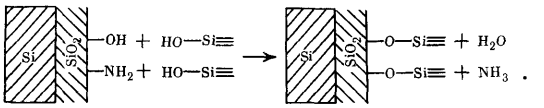
According to this mechanism, the terminal hydroxy-groups of the oligomer are retained and can participate in the subsequent polycondensation or cocondensation with epoxide resins. Although the result of the analysis of the reaction products for molecular hydrogen is not quoted in the above study[234], the proposed mechanism has been confirmed by other data[233].

3. The Mechanism of the Interaction of Oligo- and Polyorganosiloxane with the Surface of Single Crystal Silicon and the Possibility of the Polymerisation Filling of Polyorganosilasesquioxanes

It was noted above that among polyorganosiloxanes, the best dielectric characteristics, not inferior to the characteristics of amorphous silicon dioxide, are those of polyorganosilasesquioxanes with $F \geq 3.0$ and small substituents, as a rule methyl substituents. PMSSO have therefore found applications in semiconductor devices and integrated circuits as passivating films, active dielectric layers, protective coatings, and masks in doping processes[56,108,110,111]. The advantages achieved by employing POSSO are associated not only with the simplification of the technology of the formation of the layers and films directly on the surface of the semiconductor single crystal and with their non-crystallisability[89, 110,111] but also with the possibility of the passivation of the surface of a single crystal when the latter interacts with POSSO as a result of the decrease of the concentration of the surface states (of the type of surface impurities and point defects). The phenomenon is caused by the occurrence of a complex set of chemical reactions on the surface of the single crystal.

We may recall that in the single crystal silicon–amorphous silicon dioxide system there is a transition layer at the interface, which is completed by a thin layer of the natural oxide growing on the surface of the silicon single crystal at room temperature in air. The thickness of this layer varies in the range 15–30 Å as a function of the material of the single crystal and external conditions. The nature of the interphase states is determined by the supersaturation of the surface layer of the single crystal with oxygen, the presence of stresses due to the incompatibility between the surface layer subjected to stretching stresses and the pseudocoesite layer subjected to compressive stresses, as well as the presence of microcrystallite inclusions and discontinuities in the intermediate $SiO_x (x < 2)$ layer. Furthermore, the concentration of the interphase states increases appreciably due to the presence on the single crystal surface of interstitial silicon atoms—adatoms, vacancies, and their clusters[108] and also as a consequence of the presence of hydroxy-groups and other functional groups (for example, NH_2) and impurities sorbed on the silicon dioxide surface. The influence of the interphase state on the electronics of the semiconductor–dielectric structures has been described in detail in the literature[151]. The self-limited ordered clusters examined in Section II [20] have structures very similar to those of POSSO and the stresses arising in the transition region may partly relax as a result of the cleavage of the Si–O bond via a free-radical mechanism[166].

On the basis of the data described above, we shall consider the mechanism of the interaction of PMSSO with the natural oxide film. The interaction with the oligomer melt begins from the oxide surface via the functional groups[169] in accordance with the scheme



The removal of volatile reaction products from the surface layer does not present difficulties under these conditions. The next stage, initiated by free-radical states present in the pseudocoesite layer, consists in the incorporation of the substance of this layer in the polymer matrix, which is accompanied by an increase of the overall functionality of the material. Bearing in mind the ratio of the amounts of the interacting OMSSO and the amorphous silicon dioxide, which can be readily found from the relative thicknesses of the layer—on average a ~20 Å SiO_2 layer (including the ~10 Å SiO_x layer with $x < 2$) and a ~5×10^4 Å OMSSO layer—it is easy to understand why the overall increase of functionality is small.

The next, concluding stage is associated with the polycondensation of the oligomer at 180–200 °C and the formation of an infusible and insoluble skeletal polymer on the surface of the support. The processes involving the incorporation of a silicon dioxide layer in the overall polymer structure are completed in this temperature range and there is a sharp decrease of the concentration of hydroxy-groups. The inter-relation of the oligomer–polymer–synthetic silicon dioxide (from the polymer)–fused quartz structures and the character of the reactions can be seen from a comparison of their infrared spectra illustrated in Fig.9. The presence of a small but finite number of hydroxy-groups in the polymer formed ensures the possibility of the generation at temperatures below 200 °C of ionic states in the relaxed POSSO matrix and of the competition between heterolytic and homolytic silanol bond dissociation processes at temperatures of 200–400 °C; above 400 °C, the latter process becomes dominant[108]. These processes are described by the equations of the formation reactions of ionic states:

$$\equiv Si{-}O{-}H \rightarrow \equiv Si{-}O^{\ominus} + H^{\oplus} ,$$
$$\equiv Si{-}O{-}H \rightarrow \equiv Si^{\oplus} + HO^{\ominus} ,$$

and free-radical states:

$$\equiv Si{-}O{-}H \rightarrow \equiv Si{-}O^{\cdot} + H^{\cdot} ,$$
$$\equiv Si{-}O{-}H \rightarrow \equiv Si^{\cdot} + HO^{\cdot} .$$

The terms "ionic state" and "free-radical state" imply that the charge or the unpaired electron on the silicon or on what have become non-bridging oxygen atoms are bound and localised in a certain element of the matrix[108] and their movement involves the mechanism of the exchange interaction with the nearest neighbours[160,170]. The non-chain products of the cleavage of the silanol bonds, namely $HO^{\ominus}$, $H^{\ominus}$, $HO^{\cdot}$, and

H$^{\cdot}$, are not localised, possess a definite mobility in the siloxane matrix, and are capable of interacting with POSSO via a mechanism involving ring opening[108,170]:

$$\equiv Si-O-Si\equiv + HO^{\ominus} \rightarrow \equiv Si-O^{\ominus} + \equiv Si-OH \ ,$$
$$\equiv Si-O-Si\equiv + H\dot{O} \rightarrow \equiv Si-\dot{O} + \equiv Si-OH \ ,$$
$$\equiv Si-O-Si\equiv + H^{\oplus} \rightarrow \equiv Si^{\oplus} + \equiv Si-OH \ ,$$
$$\equiv Si-O-Si\equiv + H^{\cdot} \rightarrow \equiv \dot{S}i + \equiv Si-OH \ .$$

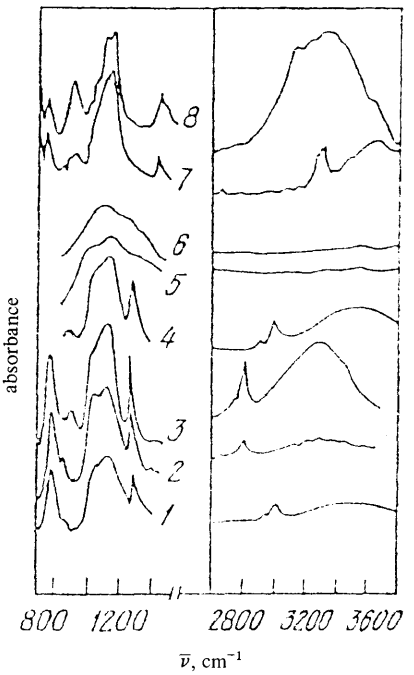


Figure 9. Comparative infrared spectroscopy of polyorganosilasesquioxanes, synthetic silicon dioxide, and fused quartz[89,110,111,120,275]: 1)–3) OMSSO, $F = 3.25$, $F = 3.14$, and $F = 3.0$ respectively; 4) PMSSO, $F = 3.0$ (prepolymer); 5) PMSSO annealed in air at 700 °C for 1 h; 6) fused quartz; 7) octaphenylcyclo-octasilasesquioxane; 8) tetrahydroxytetraphenylcyclotetrasiloxane.

Bearing in mind that the macroscopic mobility of fragments of the three-dimensional siloxane chain in which the ionic or free-radical states are localised is zero at a concentration of hydroxide ions or hydroxy-radicals $c_{HO^{\ominus}} \leq a$ or $c_{HO^{\cdot}} \leq b$ (whereupon the probability of their recombination is low), one may assert that, up to a certain consideration limit, the processes involving the generation of ionic or free-radical states in the matrix predominate over their recombination processes.

The structural defects on the surface of a dislocation-free silicon single crystal are point defects of the type of interstitial atoms, vacancies or their clusters. We shall examine only individual defects, which does not alter the overall picture. In the case of a simplified model of a section of the single crystal silicon surface with two point defects—a vacancy and an interstitial atom—it has been estimated that the long-range influence of these defects in the POSSO matrix extends over more than 54 Å [108] on the basis of the data of Panteleev and Opulich[242], which in the case of polyphenylsilasesquioxane, with the interchain distance $d = 12.8$ Å,[89] covers, in the direction at right angles to the interface, more than four molecular layers and, for PMSSO with $d = 8.4$ Å, more than six molecular layers.

The silanol bonds may be cleaved under the influence of the gradient of the electromagnetic field of the point defects consisting of an interstitial atom or a vacancy (similarly to the situation discussed in the study of Vorotyntsev and Kornyshev[240]). The gradients of the electromagnetic field of point defects constitute at the same time the driving force of the migration of the ionic and free-radical states in the organosiloxane matrix. Bearing in mind the paramagnetism of the vast majority of the single crystal silicon surface states considered, their interaction with the ionic states emerging at the interface has been shown[108] to take place as a result of charge transfer:

$$\equiv Si-O^{\ominus} + \{R^{\pm}\} \rightarrow \equiv Si-O^{\cdot} + \{R^{\pm} \cdot \bar{e}\} \ ,$$
$$\equiv Si^{\oplus} + \{R^{\pm} \cdot \bar{e}\} \rightarrow \equiv \dot{S}i + \{R^{\pm}\} \ ,$$

where $\{R^{\pm}\}$ represents a semiconductor in the form of an infinite donor–acceptor reservoir relative to a single ion.

The charge transfer results in the formation of localised free-radical states capable of interacting, following a sufficiently close approach to the interface, with the unpaired electrons localised at the defects. Very few charged surface states interact directly with the ionic states emerging at the interface.

As free-radical states of the type $\equiv Si-O^{\cdot}$ approach an interstitial silicon atom on the single crystal surface, there is a possibility of its multistage interaction with three uncompensated bonds, which can be described by the following overall expression:

$$3\,(\equiv Si-O^{\cdot}) + A\{M\} \rightarrow \begin{matrix} \equiv Si-O \\ \equiv Si-O \\ \equiv Si-O \end{matrix} \!\!> Si-\{M\} \ , \qquad (3)$$

where A{M} is an interstitial atom (Si) on the surface of the single crystal {M}, which will be henceforth referred to as an adatom.

The interaction of a free-radical state of the type $\equiv \dot{S}i$ with a point defect of the type of a vacancy V{M} can be described analogously:

$$\begin{matrix} \equiv Si-O \\ \equiv Si-O \\ \equiv Si-O \end{matrix} \!\!> \dot{S}i + V\{M\} \rightarrow \equiv Si-O-\{M\} + 2\,(\equiv Si-\dot{O}) \ .$$

Bearing in mind that the number of vacancies in the atomic plane of a dislocation-free single crystal is approximately equal to the number of adatoms[108,243] and that the number of free-radical states of the type $\equiv \dot{S}i$ generated in the organosiloxane matrix is approximately equal to the number of states of the type $\equiv Si-O^{\cdot}$, the overall annihilation process in the interaction of free-radical states of the amorphous organosiloxane matrix and surface states of the type of the point defects of the silicon single crystal can be described by the equation[108]

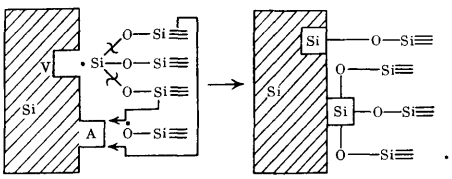
$$\equiv \dot{S}i + V\{M\}\,A + \dot{O}-Si\equiv \rightarrow \equiv Si-O-\{M\}-Si\equiv \qquad (4)$$

However, since the Si–Si bond formed as a result of reactions (3) and (4) in the systems considered (especially under the conditions of the saturation of the surface layers of the silicon single crystal with oxygen) is energetically unfavourable, it either dissociates or is oxidised further to form a siloxane linkage.

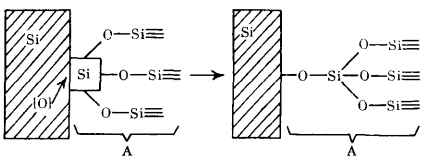
The mechanisms examined together with the processes involving the dislodging of the impurities sorbed on the surface of the natural oxide[54,169] and their sorption by the

amorphous phase of the dielectric can explain the decrease of the concentration of the surface states of single crystal silicon when it is protected by a POSSO film[108-111].

On the basis of the data of Andrianov et al.[108], the following mechanism for the interaction of a single silicon crystal with POSSO has been put forward[110,111]:



Taking into account data[239] for the atomic state of oxygen in the surface layer of a silicon single crystal, this mechanism can be refined:



with an increase of the functionality of the local cluster A from 3.0 to 3.25.

The results of a study of the photothermostimulated exoelectron emission over a wide temeprature range[120] may serve as confirmation of the mechanisms of the observed decrease of the concentration of interphase states. The experimental data obtained for systems comprising a POSSO film both on normal silicon and silicon of the *n*- and *p*-types lead to the important conclusion that there are two stages in the interaction. The first stage begins at the melting point of the oligomer and terminates with its complete conversion into the polymer. It is characterised by the fixation of the surface structures and the formation of an interface and in essence constitutes a pseudoepitaxial process in which an interfacial layer is formed on an ideal single crystal surface which continues on further increase of the ideality of the surface. This is manifested by a relative independence of the intensity of the exoelectron emission of temperature on the luminescence curves. The interaction between the film and the support decreases the regularity of the POSSO structure compared with the initial material as a consequence of the interaction with the layer of the natural oxide and the dissolution of the impurities sorbed by the natural oxide on the surface of the single crystal in the OOSSO melt with their subsequent sorption in the bulk of the infusible polymer[169,170] via the mechanisms presented above.

The temperature of the onset of the second stage of the interaction of the finished polymer with the support depends greatly on the defectiveness of the surface and the character of the impurities in the bulk of the silicon. For normal silicon, this temperature is in the range 377–393 °C and diminishes with increase of the concentration of the surface point defects. The structure of the spectrum of the photothermostimulated exoemission is in this case fairly simple and is characterised by a single broad luminescence band. Two emission maxima are observed for *n*-type silicon in the range 347–377 °C with a separation $\Delta T = 18$ °C and for *p*-type silicon there are two maxima in the range 393–423 °C with a separation $\Delta T = 7$ °C. This result can be explained by the different effects of the donor and acceptor impurities on the charge state of the surface point defects and the surface as a whole and is due to the different efficiencies of the annihilation of ionic and free-radical states of the type $\equiv Si^{O}$ and $\equiv \dot{S}i-O^{O}$, on the one hand, and $\equiv \dot{S}i$ and $\equiv Si-\dot{O}$, on the other.

The mechanism of the interaction of oligo- and poly-organosilasesquioxanes with single crystal silicon described[100,111,140,169,170] is useful in the development of a technology for polymerisation-filled composites, with dielectric characteristics modifiable within wide limits, on the basis of POSSO and transition metal oxides such as titanium dioxide or tin dioxide. In this case the filler particles can be regarded as single crystals. The activation of the filler surface makes it possible to increase the concentration of the active functional groups and to obtain a polymerisation-filled POSSO composite with 70 wt.% of tin dioxide as the filler bound to the polymer matrix via Si–O–Sn linkages.

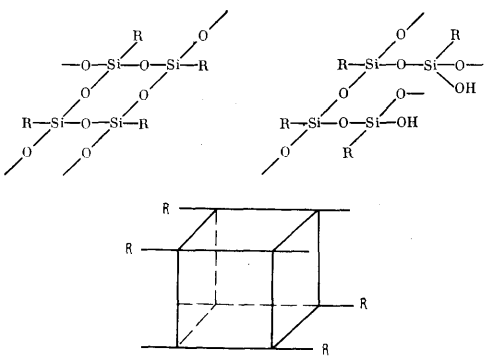
VI. THE STRUCTURE OF CYCLIC ORGANOSILASESQUIOXANES, OLIGO-ORGANOSILASESQUIOXANES, and POLY-ORGANOSILASESQUIOXANES

The discovery of the relation between the molecular structure and macroscopic characteristics of polymeric dielectrics[89,149,152] has stimulated studies on the molecular structure of POSSO and modified materials based on them. However, their electrical strength[244] and other electrophysical parameters depend greatly also on the character of the disorder of the condensed phase, which is analysed either in terms of the radial distribution function for monatomic materials (its application to a diatomic material[245] can lead to inaccuracies) or in terms of the atomic pair function[246]. The degree and character of the possible ordering in disordered tetrahedral structures, which are of definite interest for comparison with siloxane matrices, have been examined in two investigations[18,247].

Polyorganosiloxanes are tetra-atomic systems and accurate quantitative X-ray diffraction methods for the analysis of amorphous solids are inapplicable to their investigation. However, a number of studies have been carried out in order to obtain X-ray diffraction data to determine the most general characteristics such as the average interchain distances[82,116,124,248-250].

1. The Molecular Structure of Oligo- and Poly-organosilasequioxanes. The Statistical Copolymer Model

In order to reach a conclusion about the supermolecular organisation of a condensed non-ordered phase when limited structural data are available, it is necessary to have data on the molecular structure. The molecular structures of oligo- and poly-organosilasesquioxanes have been investigated[89] by infrared spectroscopy and NMR for a series of specimens with different functionalities obtained under different rigorously controlled conditions. The reaction products consisted of a complex mixture of oligomers whose MWD was determined by the process conditions. In addition, a study was made of the products of the thermal polycondensation of the oligomers obtained, of the high-temperature annealing of the polymers in air at 700 °C, and, for comparison, of amorphous silicon dioxide. The results of the infrared spectroscopic investigation of the specimens (Fig.9)[89,109-111,120] show that the structure of the molecules of oligo- and poly-organosiloxanes can include both planar and large three-dimensional cyclic units predominantly of the T_8 type.



The molecules of oligomers can incorporate all three types of cyclic units. The absorption band in the range 915–930 cm^{-1}, whose intensity decreases with decrease of the content of hydroxy-groups and can be assigned, according to Andrianov et al.[89], to the deformation vibrations of the OH group in a planar ring, in agreement with other data[251], is of definite interest.

Low-resolution NMR spectra[89] also indicate the absence of both intermolecular and intramolecular hydrogen bonds from the test specimens. The predominantly dispersion character of the intermolecular interaction is indicated, apart from the low mechanical characteristics, also by X-ray diffractometer data. All the oligo- and poly-organosiloxane specimens investigated are amorphous to X-rays regardless of the method of their preparation and the heat treatment conditions[89,110,111,120]. The maximum of the first amorphous halo occurs at 8.4 Å for oligomethylsilasesquioxanes regardless of their functionality $F = 3.0–3.25$; for oligophenylsilasesquioxanes, the maximum is at 12.8 Å, which agrees well with the value ~13 Å quoted in other studies[104,250], etc.

The data enumerated permit certain conclusions about the molecular structure of oligo- and poly-organosilasesquioxanes[89,109–111,120,140]. The structure can be described statistically by an average model incorporating structures of the T_8 type, in completely closed T_8 rings, closed and open rings of the type T_6 and T_4, and also statistically distributed OH groups. Here it is necessary to take into account the possibility of the involvement of fragments of smaller rings in the formation of the structures of larger rings. This model corresponds to the arrangement of the macromolecule in the form of a large helix[140] in which there are breaks in the rings ensuring the relaxation of structural stresses and segmentation at intervals corresponding to approximately one turn of the helix, which is consistent with the measured dimensions of the Kuhn segment[116]. If the analogy between OOSSO and POSSO, on the one hand, and silicates with large cations, on the other, is extended, one can postulate that the polyphenylsilasesquioxanes obtained under the conditions of the studies of Janin and Guyot[99] and Andrianov et al.[78] should resemble the xonotlite ribbon-like structures having unsatisfactory dielectric properties, while the OOSSO obtained under the conditions of the studies of Kamaritskii et al.[88] and Andrianov et al.[89] resemble more closely chrysotile asbestos or, what is even more likely, potassium cerium silicate with a three-dimensional anionic skeleton, namely $K_2CeSi_6O_{15}$,[252,253] whose structure constitutes a new example of an anionic purely silicon–oxygen skeleton made up of xonotlite ribbons which extend along the y axis and undergo a significant deformation due to the puckering of the rings and their mutual rotation in the xy plane. Direct condensation of the strips at the $z = 0$ and $z = 1/2$ levels leads to an open network of centrosymmetric eight-membered (xonotlite) rings and six-membered (lovozerite) rings perpendicular to them. When the rings are joined together, helices made up of tetrahedra around parallel z axes 2_1 arise. The formula of the skeletal anion does not have the standard form $[SiO_2]_{\infty\infty\infty}$ and is in fact $[Si_2O_5]_{\infty\infty\infty}$ owing to the presence of a single free O atom in each tetrahedron. In the formula of this silicate with eight-membered rings there are only six Si atoms, because the initial pair of atoms in the second ring constitutes the final pair of the first ring.

On the basis of the results of a number of investigations[78,79,88,89,104,110–113,120,128,140], we proposed a statistical copolymer model for OOSSO and POSSO, for both cyclic three-dimensional cage-like organosilasesquioxanes and for the compounds with the ladder structure. In the study of ladder POSSO, it was observed[78] that, on formation of ladder macromolecules with a double stranded cyclolinear structure, one of the essential stages involves the rearrangement of the cyclic three-dimensional ("cage-like") fragments. It has been pointed out that polyphenylsilasesquioxanes have a high degree of order only in individual polycyclic sections distributed statistically along the chain. Furthermore, it has been stated directly[104] that the elementary units of the macromolecular chain are polydisperse as regards dimensions. The fact that in the hydrolytic cocondensation of trichlorophenylsilane and trichlorovinylsilane in their mixture there are no products of their separate hydrolysis, mentioned above, is also striking[79].

2. The Study of the Phase Structure of Cyclo-, Oligo-, and Poly-organosiloxanes. The Interrelation of the Structural Forms

As stated above, the non-crystallisability of POSSO, noted in a number of studies[56,88,89,109–112,120,140,165], limits the applicability of diffraction methods also in the study of their structures[89]. The non-crystallisability of POSSO is determined to some extent by the skeletal structure of their molecules, because the possibility of a three-dimensional rearrangement of molecular fragments, requiring the dissociation of at least two of the three siloxane linkages, is virtually ruled out. The crystallisation of the synthetic material obtained by the thermal oxidation of POSSO, which inherits the molecular structure of the latter and whose composition $\{SiO_2\}_n$ is identical with that of silicon dioxide, requires the dissociation of $3n$ Si–O bonds[111].

A genetic approach to the morphological changes in siloxanes has been proposed[112], starting with the simplest rings [tetraphenyltetrahydroxycyclotetrasiloxane (T_4), its dimer hexaphenyltetrahydroxybicyclotetrasiloxane $(T_4)_2$, and octaphenylcyclo-octasilasesquioxane[159] (T_8)] and proceeding via the corresponding oligomers and pre-polymers to give infusible and insoluble polyphenylsilasesquioxanes. The compounds T_4 and T_8 are crystalline substances and X-ray diffraction data have been obtained for them by a standard diffractometric method using Cu K_α radiation and have been checked by an especially developed photomethod[254].

According to Andrianov et al.[89], neither oxidation-reduction nor disproportionation processes take place during the hydrolytic condensation of OCS. In the products of the hydrolytic condensation of OCS each silicon atom is linked to three oxygen atoms and to one organic group. Furthermore, it was shown in the same study[89] that the large molecules have a cyclic three-dimensional structure and consist mainly of alternating large (T_8) and small (T_4) rings. It follows from this that the problem of the description of the structure of oligo- and polyorganosilasesquioxanes can be reduced to a quantitative analysis of the contents of the above structural fragments.

A method based on the Selyakov–Scherrer spreading of the polycrystalline reflections of the T_4 and T_8 rings and on a graphical comparison of the curves thus obtained with the experimental curves for oligomers and polymers with different degrees of condensation has been proposed[112]. This procedure is carried out taking into account the influence of termination, in terms of the scattering angles allowed for, on the amorphous halo patterns[255]. The characteristics of the variation of the structural forms between two probable structural elements can be readily traced from the change in the positions of the first amorphous haloes of the oligomeric and polymeric materials; on the basis of these data, a nomogram has been constructed[112] for the quantitative analysis of the contents of the T_4 and T_8 structural fragments in macromolecules. This approach can be used also in the study of other polymers[256].

The presence of cyclic structures in amorphous polyorganosiloxanes makes it possible to discuss the results for crystalline cyclic organosilicon compounds[159,257–262]. X-Ray diffraction studies on the large rings of organosilasesquioxanes have been carried out[159–200,263–265]. In order to establish a relation between the non-equivalence of the silicon atoms and the distortion of the silicon–oxygen skeletons in ethyl- and vinyl-octacyclo-octasilasesquioxanes and to refine the structure of T_8, they were investigated by high-resolution NMR in the solid state[266]. The study of the infrared spectra[267], mass spectra[268], and volatility[269] made it possible to revise their molecular structures and to permit the development of a technology for their application. A study[143] involving the measurement of the vapour pressures of a series of OOSSO is also of interest in this sense.

VII. THE ADHESION CHARACTERISTICS OF LAYERS AND COATINGS BASED ON POLYORGANOSILASESQUIOXANES

The physicomechnical properties of POSSO have been examined in a number of studies[194,198,211,212,270]. One of the most important properties of a coating must be its effective adhesion to the support. It is known that adhesion depends on a multiplicity of factors and is determined by the properties of both the adhering substance and the substrate. A study has been made[212] of the dependence of the adhesion strength of a layer of POSSO on various supports on the chemical structure and the technology of the preparation of the film and of the adhesion properties of coatings based on polymethyl-, polyvinyl-, polymethylvinyl-, polymethylphenyl-, and polydichlorophenylmethyl-silasesquioxanes, obtained from solutions of the corresponding oligomers at different concentrations in the range 10–25 wt.% in solution in the 1:1 acetone–toluene mixture, which made it possible to obtain films of different thickness (ranging from 1.0 to 6.0 μm). A polished steel support proved to be most suitable for tests on adhesion strength. At the same time measurements were made of the dielectric characteristics of the material. At a concentration of the oligomer solution below 10 wt.%, there was almost no adhesion between the plates, which can apparently be explained by the impossibility of the formation of a monolithic film between them.

The adhesion strength of various POSSO in relation to a steel support increases, other conditions being equal, with increase of the oligomer concentration, reaching a limiting value at an OOSSO concentration of 20 wt.% and then remaining almost unchanged. The degree of adhesion depends strongly on the nature of the organic substituents at the silicon atoms and also on the conditions in the heat treatment of the specimens.

The adhesion strength of POSSO is definitely influenced by their functionality. The increase of the overall rigidity of the polymer film with increase of the functionality from 2.9 to 3.0 impairs the adhesion strength. This effect can be associated with the increase of the contribution of the relaxation phenomena with increase in elasticity and also with the change in the number of effective contacts at the adherent–substrate boundary.

There is a correlation between the adhesion strength and the angle of wetting of various supports by solutions of the corresponding OOSSO. It has been established[212] that oligophenylsilasesquioxanes are characterised by increasing wetting angles on various supports and that an increase of concentration entails an increase of the wetting angle. These features are common to a series of surfaces: steel, chromium-plated steel, single crystal silicon, glass, and gold-plated sital. Furthermore, it is known that the wettability of a surface improves (the wetting angle diminishes) with improvement of the quality of the preparation of the surface—a polished surface is wetted more effectively than a non-polished surface.

In the study of adhesion properties in a support–POSSO system account must be taken of a series of factors. The surfaces of the majority of supports are coated by a more or less thin layer of oxide and in these cases the properties of the surface hydroxy-groups are determined to a decisive extent by the nature and structure of these oxides[241]. The presence of reactive hydroxy-groups in OOSSO improves the adhesion of the dielectric coating to the supports. In this case, if the hydroxy-groups on the surface of the support are reactive with respect to the silanol bonds of the oligomer, condensation and grafting of the molecules to the surface take place. On the other hand, if the surface layer consists of adsorption water, there is a possibility of interaction with the rings, leading to the rupture of the surface layer of the oxide and then to direct interaction of the organosiloxane with the support, as happens in the aluminium–amorphous SiO_2 system[271].

The modification of POSSO both at the molecular level (for example, by introducing the aluminium heteroatom directly into the siloxane chain[128]) and in the bulk phase level exerts a major influence on the adhesion properties of such systems. However, one must then bear in mind that the bulk-phase modification usually leads to an appreciable impairment of the overall dielectric characteristics of the materials.

VIII. ELECTROPHYSICAL PROPERTIES OF POLYORGANOSILASESQUIOXANES AND MODIFIED MATERIALS BASED ON POLYORGANOSILOXANES

All the preceding discussion of both the synthesis and the technology of the preparation of oligo- and poly-organosilasesquioxanes and modified materials based on polyorganosiloxanes as well as their structure and physicomechanical characteristics was based on a single postulate, namely that the ultimate result must be the creation of materials with specified electrophysical, namely dielectric, properties: at the same time their compatibility with both traditional semiconductors[108–111] and with special purpose semiconductors, particularly organic semiconductors[1] as well as adequate advantages in the technology of electronic instrument making must be ensured. We shall consider the two most important methods for the investigation of the electrophysical properties of dielectrics—dielectric spectroscopy and polarisability of polyorganosilasesquioxanes and related materials,

the discussion being preceded by certain new ideas concerning the mechanism of the transport of current carriers in disordered dielectrics[272].

1. The Tunnel Electrical Conductivity of Disordered Dielectrics

In amorphous materials the lack of structural order induces the localisation of electronic states and determines the character of the conductivity of disordered polymeric dielectrics[272]. Electron transfer via localised states is described by methods of the permeation theory[273], which can be explained by a simplified model. The quantum nature of the jump conductivity permits the hypothesis of electron tunnelling between localised states. An attempt has been made[272] to develop a tunnel model of the electrical conductivity of disordered systems and to test it experimentally on amorphous polymeric dielectrics.

The analogous character of the calculated and experimental relations between the conductivity and the concentration of localisation centres confirms the validity of the model involving electron transfer via localised centres in polymeric disordered dielectrics[274].

The tunnel model proposed[272,274] leads to an expression for the electrical conductivity which agrees with the results of the permeation theory[273]. This model makes it possible to explain the deviations of the experimental results from calculations based on the permeation theory. It can be used to describe the electrical conductivity of disordered polymeric dielectrics.

2. Dielectric Spectroscopy of Polyorganosilasesquioxanes and Modified Materials based on Polyorganosiloxane

The quality of a dielectric material should be assessed and the scope and regions of its applications should be determined not so much in terms of each of the parameters enumerated at the beginning of the present study as, firstly, in terms of the sum of the dielectric properties (naturally subject to the condition that none of the parameters determining the usefulness of the material is below the lower limit), secondly, in terms of the possibility of altering within the required limits one or several parameters in accordance with the functional purpose of the material without a significant impairment of the sum of its dielectric properties, and, thirdly, in terms of the stability of both functionally significant parameters and the sum of the dielectric properties in relation to external influences[110,111], usually the influence of temperature or moisture content or their combined influence. The influences of radiation, gaseous atmospheres[56], acids, salts, bases[128], etc. must be regarded as other external influences of practical importance but encountered more rarely.

The dielectric parameters of PMSSO differ little from the characteristics of amorphous SiO_2. However, it has been shown[88] that, when the hydrolytic condensation of TCMS is carried out under otherwise optimal conditions, the values of tan δ and ε at different frequencies depend on the temperature of the synthesis. The knowledge of these relations makes it possible to obtain materials with specified characteristics and the modification is carried out using the differences in the course of the polycondensations of oligomers at different temperatures[275]. The dielectric properties can be altered by this procedure only within certain limits.

Significantly greater changes in the parameters of the substance can be achieved by chemical doping (or by the introduction of a heteroatom) directly into the siloxane chain[120,211], or by employing a molecular fragment whose chemical nature is different from that of the organosiloxane matrix[194], or by the structural modification of polyorganosiloxanes. Better results can be achieved by the last method than by chemical doping, but, within fairly narrow limits of the modifier concentrations, all the relations governing the properties of the material (both electrophysical and physicochemical) pass through a sharp maximum with increase of the concentration of the dopant owing to the appearance of the heterophase of the modifier or its reaction products. Although the introduction of a heteroatom into the siloxane chain causes a smaller change in the dielectric characteristics, it leads to the precipitation of the heterophase and ensures a high resistance to external influences, since the modification is carried out at the molecular level.

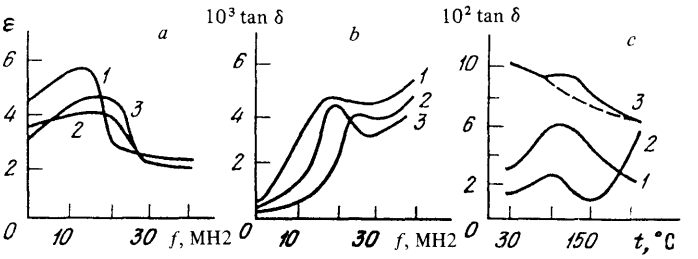


Figure 10. Dielectric spectroscopy of polyorganoaluminosiloxanes: *a*) frequency dependence of the dielectric constant ε; *b*) frequency dependence of the tangent of the dielectric loss angle tan δ; *a* and *b*: 1) MM-12; 2) MV-12; 3) MF-13.2; *c*) temperature dependence of tan δ for MM-12 at different frequencies (Hz): 1) 5×10^4; 2) 2×10^6; 3) 4×10^6.[128]

The dielectric parameters (ε and tan δ) of films based on polyorganoaluminosiloxanes have been investigated[128] over a wide range of frequencies and temperatures (Fig.10). Calculation of the relaxation time from the frequency of the maximum of the dielectric losses (Fig.10*b*) yields $(6-8) \times 10^{-9}$ s, which is characteristic of dipoles or dipolar complexes with a high molecular weight. The temperature variation of tan δ (Fig.10*c*) has a characteristic dielectric losses maximum at a temperature which is higher the higher the frequency, while ε initially increases with temperature, which can be accounted for by the increase of the mobility of the fragments of the polymer molecules resulting in a facilitation of the orientation of the dipoles. On further increase of temperature, the intensification of thermal vibrations reduces the degree of order and ε falls after it has passed through a maximum. Films based on polyorganoaluminosiloxanes have fairly low values of tan δ over a wide temperature range up to 350–400 °C, which makes it possible to classify them as high-temperature dielectrics. At low frequencies the values of ε and tan δ diminish with increase of the aluminium content in the siloxane chain, which is apparently associated with the increase of the rigidity of the polymer structure, while at high frequencies, where polyaluminosiloxanes can be regarded as non-polar dielectrics, ε and tan δ are almost independent of the aluminium content in the polymer. The electrical strength of such films increases slightly with increasing aluminium content in the siloxane matrix.

3. The Polarisability of Modified Polyorganosiloxanes. The Electret Effect

The polarisability of dielectrics is one of their fundamental characteristics which makes it possible to discover the kinetic relations governing the accumulation and dissipation of the charge. All the effects occurring on active dielectrics—the charge bond, the electret effect, and others—are determined, when other dielectric properties are satisfactory, by their polarisability.

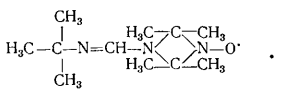
The results of studies of the processes involving the accumulation and dissipation of charges in electrets for various methods of imparting an electric charge (thermo-, electro-, and tribo-electrets) and studies of the influence of a large number of external stabilising and destabilising factors (acoustic, thermal, electromagnetic, and combined influences) have been described[123]. It was established that, when electrets, including PMSSO, are subjected to an acoustic influence, the spectrum of the relaxation times of the charges changes and the relaxation times τ diminish to a greater extent the more prolonged the influence. It has been noted that electrets with a higher level of charge (>100 V) are less stable when subjected to an acoustic influence of long duration. Comparison of different influences leads to the following relation between the relaxation times:

$$\tau(\text{control}) \gg \tau(\text{acoustic}) \gtrsim \tau(\text{electromagnetic}) > \tau(\text{combined}).$$

In a polarised dielectric medium the phase velocity V_ϕ of ultrasound increases with increase of the space density of the electric charge Q_V. For example, in poly(methyl methacrylate) a change in Q_V by 1×10^2 C m^{-3} alters V_α by 10%.[193]

The characteristic features of the electret effect are investigated by studying the spectrum of the electric states of localised charge carriers in polarised dielectrics. Specific modification of the capture centres by the introduction of donor–acceptor additives[165,211] into the polymer matrix alters the spectrum of the charge relaxation times of the electret and the differentiation of additional TSD current peaks makes it possible to relate models of the capture centres to the structure of the polymer at the molecular level[276].

Thus the kinetic characteristics of electrets based on PMSSO and modified materials obtained by the chemical polycondensation of OMSSO and an oligomer in the presence of an electron-donating additive in the form of a long-lived free radical R have been studied[165]:



The concentration of this radical is 0–10 wt.%. A discrete measurement of the electret potential difference $U_k(t)$ was carried out. In order to compare the characteristics of electrets with different initial potential differences $U_k(0)$, the time variation of the dimensionless quantity $k = U_k(t)/(U_k(0)$ was analysed. The OMSSO polycondensation phenomena and the structural changes in the specimens on polycondensation were investigated by gravimetric, X-ray diffraction, and EPR methods. In the course of the increase of the polarisation potential U_n from 0.5 to 4.0 kV, a change in the sign of $U_k(0)$ as a consequence of the reverse discharge effect was observed. The study of the structural changes in the oligomer following the introduction of R demonstrated an increase of the average interatomic distances r and Δr and a redistribution of the contributions of the scattered intensity owing to the increase of the contribution of scattering by atoms and the decrease of the contribution of scattering by chains. The magnitude of the effect is proportional to the concentration of the radicals R. During polarisation, the influence of the injected radicals R passes through a minimum[165] because they are involved in at least two competing reactions—chain termination and the grafting of the radical to the groups around the siloxane chain. The latter reaction determines the polarisation of the polymer and the generation of a stable electret state.

IX. CONCLUSION

The wide range of applications of highly functional organosilicon polymers[42,46,49–54,56,57,75,98,107–111,120,128,151,152,165,190,193,208,215,217,234,277] can be supplemented by applications in which their dielectric properties play an important but not a decisive role and the entire set of the useful properties of materials based on them is employed[194,278,279]. Clearly such polymers have a whole series of other useful qualities, among which one may mention thermal, plasma, and tracking stability, but evidently their joint survey within the framework of a single article is impossible.

The methods developed for the conversion of soluble and fusible oligomers[49,56,57,75,88,104,108–111,120,128,140,165,169,170,211,212,275] lead to the formation of polymers with the required properties only when oligomers with rigorously defined properties are used as the starting materials and with a rigorous maintenance of specific conditions in the polycondensation process. The presence in the oligomer of even filterable gel particles results in a sharp impairment of the dielectric characteristics of materials based on POSSO. Highly functional oligomers are metastable and, depending on the degree of purification and the storage conditions, their properties deteriorate more or less rapidly and they give rise to products with a wider range of MWD, up to the formation of gel particles.

One of the most important stages in the technological chain leading to the preparation of the materials is therefore the first stage in which soluble and fusible oligomers with a specific set of physicochemical characteristics (average molecular weight, MWD, the number of hydroxy-groups, the content of limiting impurities, etc.) are formed[89,92,93]. The formation of such oligomers requires an appropriate organisation of the technological process. The chemical nature of the hardening processes and of the interaction with the supports is also determined by the technological conditions. Thus the formation of materials based on metastable substances is determined at the technological level.

The dependence of the dielectric properties of materials on the molecular and phase structure of the polymer, on the one hand, and the distinct dependence of its structure on the synthesis conditions, on the other[70,88], show that the quality of the polymeric materials is in many respects determined by the methods, technological procedures, and the conditions in the preparation of oligomers as well as the monitoring of the intermediate products, since the parameters of the future material and the quality of the articles made from it are in fact determined at this level.

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