Translated from *Uspekhi Khimii*, **44**, 468-501 (1975) U.D.C. 547.927.41

Advances in the Chemistry or Organosilicon Polymers

V.V.Korshak and A.A.Zhdanov

The great synthetic possibilities in the chemistry of organosilicon systems and the wide variety of their properties are discussed. The high reactivity of cyclic organosilicon systems with respect to various rearrangements and polymerisation, which gives rise to unlimited possibilities for the synthesis of macromolecular organic derivatives of the elements, is specially considered. The bibliography includes 222 references.

CONTENTS

I.	Introduction	227
II.	Linear and branched polyorganosiloxanes	227
III.	Polymers with cyclonetwork molecular structures	231
IV.	Polymers with cyclolinear ladder molecular structures	232
V.	Polymers with spirocyclic and spiroladder molecular structures	234
VI.	Polyorganosilazanes	235
VII.	Polyorganosiloxane derivatives of the elements	236

I. INTRODUCTION

In view of the successful development of the chemistry of organic polymers, chemists during the first half of the 20th century had great expectations, and not without justification, from silicon as the closest analogue of carbon. However, a more detailed investigation of the chemistry of organosilicon compounds showed that silicon is incapable of forming very long polymeric chains made up of carbon atoms (analogous to polymeric carbon chains). The idea of the formation of a polymeric chain from alternating silicon and oxygen atoms led to the discovery of a new class of high-molecular-weight compounds—polymers with inorganic principal molecular chains.

K.A.Andrianov played a leading role in formulating and developing this new field of polymer chemistry. This branch of chemistry reached the greatest development in his studies and those of his numerous students.

The development of the chemistry of organosilicon polymers began in 1937 in a study by Andrianov[1] where the possibility of the formation of polymer chains from alternating silicon and oxygen atoms was demonstrated[1,2].

The research by Andrianov's school is distinguished by an exceptionally wide range of studies and by the practical applications of most of them. The investigations by Andrianov and his students laid the foundations of the chemistry of polymeric organic derivatives of the elements, which led to the discovery of the class of thermostable polymers.

Polyorganosiloxanes were the first polymers meeting the more rigorous requirements of many branches of modern engineering. These polymers have a high thermal stability and a high resistance to moisture, are chemically inert, and resist the action of sunlight, oxygen, and ozone. The chemical compositions and structures of compounds of this class are responsible for their valuable technical properties.

In terms of structure, polyorganosiloxanes occupy an intermediate position between organic polymers and silicate structures. This class of polymers has no analogues in nature as regards composition and constitutes a truly synthetic class.

Andrianov's research in the field of polyorganosiloxanes enabled him to formulate and apply in subsequent investigations the principle of combining in the polymer chain elements with appreciably different electronegativities. This idea has been reflected in a number of Andrianov's studies in the field of polyorganosiloxanes derivatives of the elements.

During the last 15 years Andrianov carried out fundamental research in the field of non-traditional and specific structures of polymeric molecules (cyclonetwork, cyclolinear, ladder, spirocyclic, etc.) in addition to studies on the classical structures of organosilicon polymers (linear and branched). The fundamental principles of the formation of the siloxane chain as well as the chemical and physical properties of polymers of the polyorganosiloxane series have been described in a number of monographs[3-6] embracing the literature data up to 1964. The main practical applications of substances of this class have been described in other monographs[7-16]. The aim of the present review was to examine studies carried out in recent years by the Soviet School of Chemists working in the field of organic silicon chemistry and headed by Andrianov.

II. LINEAR AND BRANCHED POLYORGANOSILOXANES

The polymerisation reactions of cyclic organosilicon compounds have now acquired great theoretical and practical interest, since they provide one of the most important ways of synthesising oligomers and high-molecular-weight compounds with inorganic and organic-inorganic molecular chains[4,5]. The vast majority of initiators employed consist of compounds whose molecules contain one nucleophilic centre (for example, OH^-, $\rangle NH_2^-$, or R_3SiO^-).

Andrianov and coworkers developed methods for synthesising many-centre initiators[17]. Three-centre initiators were obtained via the scheme

$$RSiCl_3 + 3NaOSi(CH_3)_2OSi(CH_3)_2ONa \rightarrow RSi[OSi(CH_3)_2OSi(CH_3)_2ONa]_3,$$

where R = CH_3, C_2H_5, or C_6H_5. Four-centre initiators were prepared by a similar reaction:

$$SiCl_4 + 4\,NaOSi(CH_3)_2OSi(CH_3)_2ONa \rightarrow Si[OSi(CH_3)_2OSi(CH_3)_2ONa]_4 .$$

Polymerisation in the presence of many-centre initiators made it possible [17-19] to obtain high-molecular-weight polymers having a branched star-shaped molecular structure:

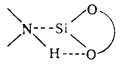
$$Si[OSi(CH_3)_2OSi(CH_3)_2ONa]_4 + n/4[(CH_3)_2SiO]_4 \rightarrow$$
$$\rightarrow Na[OSi(CH_3)_2]_lOSi(CH_3)_2OSi(CH_3)_2O\diagdown\!\diagup Si \diagup\!\diagdown OSi(CH_3)_2OSi(CH_3)_2O[Si(CH_3)_2O]_lONa \rightarrow$$
$$\rightarrow Na[OSi(CH_3)_2]_kOSi(CH_3)_2OSi(CH_3)_2O\diagup\!\diagdown \quad \diagdown\!\diagup OSi(CH_3)_2OSi(CH_3)_2O[Si(CH_3)_2O]_mONa ,$$
$$l + k + l + m = n .$$

It was established that the order of the polymerisation reaction remains constant (it is first order with respect to the monomer) with increase of the number of functional groups in the initiators from 1 to 4. When two-centre initiators are employed, there is no interaction between the terminal functional groups and polymerisation proceeds independently via both reaction centres. With increase of the number of functional groups in the catalysts, there is a gradual decrease of the rate of polymerisation owing to the resulting steric hindrance due to adjacent side chains. The determination of the average number of branching centres by Kirby's method (from viscometric and light scattering data) showed that the branching of the molecules corresponds to the structure of the initial initiator [20,21]. The polydispersity coefficient of the polymers obtained amounts to 1.89–2.90, which indicates the occurrence of interchain exchange and chain transfer reactions at high conversions of the initial cyclic monomer [21].

It is interesting that the polymerisation of trimethyltriphenylcyclotrisiloxane in the presence of branched initiators does not lead to the formation of polymers with a star-like structure [22].

Studies on the type of change in the molecular weight distribution on polymerisation of various organocyclosiloxanes established that the polymerisation of octamethylcyclotetrasiloxane in the presence of NaOH involves chain transfer processes and the resulting polymer exhibits a high tendency towards depolymerisation. In the polymerisation of the same monomer in the presence of the initiator $(CH_3)_3SiON(CH_3)_4$ (with its subsequent elimination from the reaction sphere) a polymer is formed and secondary processes (chain transfer, branching) are not observed [23,24]. When the initiator is not removed, heating of the polymer *in vacuo* from 50° to 360°C leads in this case to depolymerisation with subsequent branching of the macromolecules.

The ideas on the mechanism of the anionic polymerisation of organosiloxane rings are based on the hypothesis of the formation of complexes between organocyclosiloxanes and nucleophilic agents [4]. A series of studies [25-30] undertaken to test this hypothesis established that molecular complexes are formed between amines and cyclosiloxanes [26-28]. The lifetimes of these complexes were established by NMR and it was found that the complexes are of a type different from that postulated previously. An experimental test of the possibility of the existence of complexes of the type NH...O$\begin{matrix}\diagup Si\\ \diagdown Si\end{matrix}$ showed [29] that the formation of a complex involving bonding of this kind is unlikely. The available data suggested a quasicyclic structure for the complexes with a non-linear hydrogen bond of the type



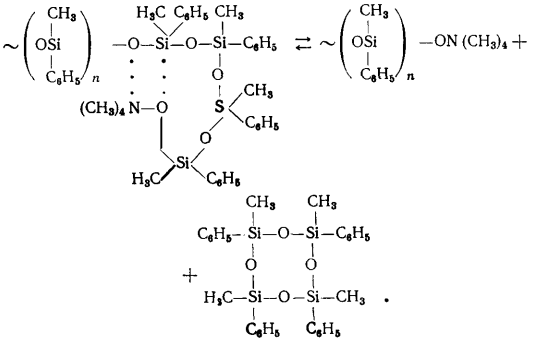
Furthermore, it was established that in the case of amines, in the absence of spectroscopically detectable admixtures of water, initiation begins with a direct attack on a ring silicon atom by the nitrogen atom [26,27].

A special series of studies in recent years was devoted to the investigation of polyorganosiloxanes containing phenyl groups at the silicon atom. Earlier investigations demonstrated an enhanced thermal stability of compounds of this class [31-33].

A study of the polymerisation of *cis*-trimethyltriphenylcyclotrisiloxane established that, owing to the high reactivity of the initial compound, the polymerisation reaction

$$[CH_3(C_6H_5)SiO]_3 + (CH_3)_4NO\left(\begin{matrix}CH_3\\|\\Si-O\\|\\C_6H_5\end{matrix}\right)_n -H \rightleftarrows (CH_3)_4NO\left(\begin{matrix}CH_3\\|\\SiO\\|\\C_6H_5\end{matrix}\right)_{n+3} -H \ldots$$

proceeds at a high rate. The depolymerisation reaction, leading to the formation of eight-membered and higher methylphenylcyclosiloxanes, proceeds at a relatively low rate and becomes appreciable only at high conversions [34-36]:

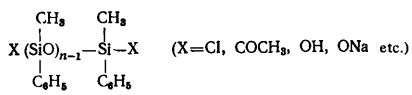


The polymerisation of *cis*-methylphenylcyclotrisiloxane in bulk, in the solid phase, and in solution leads to the formation of polymers whose actual molecular weight is appreciably lower than the molecular weight calculated from the ratio of the initiator and the cyclic compound. This can be accounted for by chain transfer reactions, traces of water and alcohols acting as chain-transfer agents. A preliminary removal from the reaction sphere of the possible chain-transfer agents leads to an increase of the rate of reaction almost by an order of magnitude and to a significant increase of the molecular weight of the resulting polymer [36].

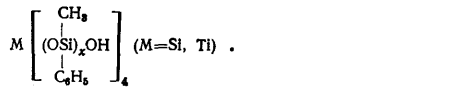
The highest yield of the polymer (95–98%) is achieved in the heterophase polymerisation of *cis*-trimethyltriphenylcyclotrisiloxane in hexane, which readily dissolves the initial cyclic compound but not the resulting polymer [37]. Side reactions, which usually lead to a broadening of the molecular weight distribution, are ruled out in this method and the polymer formed has an exceptionally low polydispersity coefficient ($M_w/M_n = 1.04$). Thermomechanical studies and studies on the hydrodynamic properties of polymethylphenylsiloxane showed that its chains are more rigid than those of polydimethylsiloxane [22].

One of the most promising procedures, which gives rise to great possibilities for controlling the composition and properties of polymers, involves the synthesis and study of linear and branched oligomers capable of conversion as a result of polymerisation and polycondensation into high-molecular-weight compounds with specified technical properties. A very important feature is that the polymerisation and polycondensation processes can be carried out directly in the finished articles.

The preparative methods devised hitherto make it possible to obtain oligomeric methylphenylsiloxanes having a wide range of terminal groups with different compositions [38,39].



The reactions of such oligomers with monomeric tetrafunctional compounds lead to the formation of oligomeric cross-like compounds with functional groups at the ends of the branches:

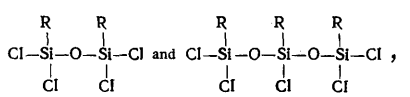


Both linear and cross-like oligomers, containing hydroxy-groups at the ends of the branches, are capable of further polycondensation. Polymers with $M = 10\,000$ and a glass point of 35 °C can be obtained from linear oligomers [40]. The condensation of cross-like oligomers proceeds via both intermolecular and intramolecular mechanisms with formation of products having complex cyclic structures [41].

The glass points of linear oligomers decrease with increase of the molecular weight, while in the case of the cross-like oligomers they depend little on the lengths of the side chain but do vary significantly as a function of the nature of the terminal functional groups [42].

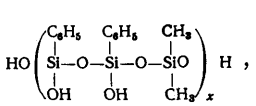
Cross oligomers with terminal hydroxyls exhibit the greatest resistance to thermo-oxidation, since on heating they form three-dimensional structures [43]. The replacement of the central silicon atom by titanium increases the thermal stability. Branched cross-like oligomers containing a certain amount of γ-trifluoropropyl groups show the greatest lubricating capacity [43].

Together with the methods of synthesis of siloxane oligomers described above, the hydrolytic condensation method merits a more detailed study, since the syntheses of the majority of organosilicon polymers are based on hydrolytic condensation processes and on the condensation of alkyl(aryl)chlorosilanes with different numbers of functional groups. The method of hydrolytic condensation in the vapour phase developed by Andrianov and coworkers [44,45] makes it possible to obtain organochloropolysiloxanes having the composition



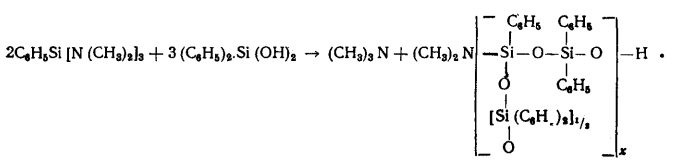
where R = C_6H_5 or C_2H_5.

The cohydrolysis of these compounds with dialkyl(aryl)-dichlorosilanes [44,46] yields oligomeric products having the composition

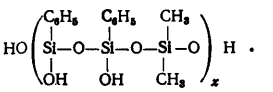


which were used to investigate the characteristics of three-dimensional polycondensation. It was established that the degree of reaction at the gel formation point and the critical branching coefficients exceed by a factor of 1.5–2 the values calculated by Flory's statistical theory. The explanation is that the condensation of the cohydrolysis products proceeds with a decrease of the number of functional groups owing to the formation of cyclic structures in the polymer units.

A similar feature was observed [44] in the condensation of aminosilanes and hydroxysilanes via the mechanism

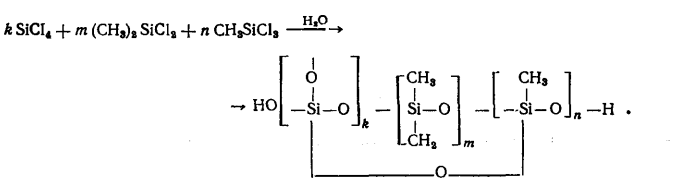


In this case the degree of reaction exceeds 90% but the resulting polymer is soluble and thermoplastic. Coatings with an appreciable resistance to petrol and oil were obtained [47] on the basis of the polyphenyldimethylphenylsiloxane oligomers investigated, which had the general formula



A study of polyfunctional systems, i.e. systems where the average number of functional groups in the initial monomers is greater than three, is of considerable interest. In such systems the C/Si ratio is appreciably reduced, which should lead to an enhancement of their thermal stability. Products of the cohydrolysis of silicon tetrachloride with dichlorodimethylsilane and chlorotrimethylsilane can serve as examples of such systems [48,49].

It was established that the yield of the gel fraction as a function of the number of functional groups in the initial system can be expressed by a polynomial equation [48], the yield of insoluble products depending also (separately) on the number of functional groups in the chlorosilanes employed. When appropriate hydrolysis conditions have been chosen, the above systems can give rise to soluble products despite the large number of functional groups in the system:



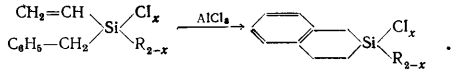
Oligomers with the above composition form protective coatings on metals, glass, and other materials. However, properties suitable for practical applications are achieved only when the average number of functional groups in the initial system is reduced to 2.6. [42]

The properties of polyorganosiloxane oligomers can be effectively modified by changing the nature of the organic group at the silicon atom as well as the number of functional groups in the initial monomers. The use of alkyl-(aryl)halogenosilanes containing 6–10 carbon atoms in the organic group attached to silicon in hydrolytic condensation reactions yielded compounds having the general formula $[RSiO(OH)]_n$, where $n = 6$ or 8 and R = i-C_5H_9, C_6H_{13}, C_8H_{17}, or C_9H_{19}. [50] These compounds condense in steps via an intramolecular mechanism. The cohydrolysis of higher alkyltrichlorosilanes with chloromethylsilanes and chlorophenylsilanes involves intramolecular condensation at a temperature not less than 60–65 °C. [51] At lower temperatures each compound is hydrolysed separately.

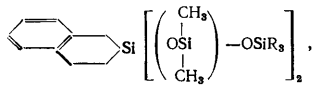
The cohydrolysis products are viscous transparent liquids, which polymerise in the presence of nucleophilic

agents. The methods devised for the synthesis of polyalkylsiloxanes served as the basis of a procedure whereby one can synthesise organosilicon liquids of new types with improved lubricating properties [52]. It was established that the introduction of units containing higher aliphatic groups at the silicon atom into polyorganosiloxane varnishes eliminates the formation of pores and bubbles when the varnishes dry out in thick layers [53].

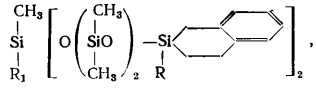
The modification of the properties of organosiloxane oligomers by altering the nature of the organic group at the silicon atom was continued in a series of studies by Andrianov on the synthesis and properties of compounds with arylalkyl groups at the silicon atom. The method of synthesis of compounds with arylalkyl groups at the silicon atom of the type $(C_6H_5CH_2CH_2)_xSiCl_{4-x}$ by the addition of chlorovinylsilanes to aromatic hydrocarbons, which was developed previously [54,55], served as the basis for the synthesis of bicyclic compounds via an intramolecular alkylation reaction [56-58]:



The introduction of silicon atoms with attached bicyclic fragments either into the siloxane chain or as blocking groups at the end of the chain yielded oligomeric products having the composition [59,60]

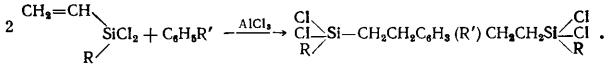


where R = CH_3, C_2H_5, or C_6H_5, or



where $R_1 = C_2H_4C_6H_4Cl$, which exhibit effective lubricating properties at high temperatures and retain them when used for a long time.

The viscosity of these compounds varies sharply with temperature and the activation energy for their viscous flow is high. Compounds suitable as high-temperature lubricants without these disadvantages were obtained by the above reaction [54,55], whereby one can also synthesise products of double intermolecular alkylation [60-62]:



Similar compounds were obtained also on the basis of compounds with two aromatic rings (diphenyl ether, diphenylmethane, biphenyl) [61]. In this case both silicon atoms add to the same aromatic ring via ethyl bridges:

$$[(CH_3)ClSiC_2H_4]_2C_6H_3—X—C_6H_5,$$

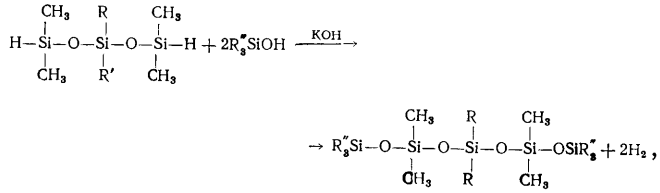
where X = CH_2 or O.

The replacement of chlorine atoms in the above compounds by trialkyl(aryl)siloxy-groups [60] yields the compounds

$$RC_6H_3\{C_2H_4SiR'_n[OSi(C_2H_5)_3]_{3-n}\}_2,$$

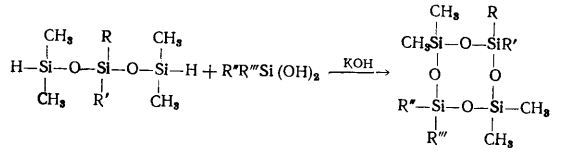
where R = H, CH_3, Cl, C_6H_5O, C_6H_5, or $C_6H_5CH_2$. They were used as the basis for high-temperature lubricants [63].

Together with hydrolytic condensation, the dehydrocondensation reaction is of interest for the synthesis of polyorganosiloxane oligomers [64-66]:



where R = CH_3 or C_2H_5, R′ = C_2H_5 or C_6H_5, and R″ = C_2H_5 or C_6H_5.

The method permits a specific heteromolecular condensation and homomolecular condensation can be prevented. This reaction can be included in the category of heterofunctional reactions, which were investigated in detail previously [3,4], but it has the advantage that it proceeds under milder conditions (40–80°C) at a high rate and with a high degree of conversion [66,67]. It also makes it possible to synthesise organocyclosiloxanes with known positions of the dialkyl(aryl)siloxane units in the ring [67]:



where R = CH_3 or C_2H_5, R′ = C_2H_5 or C_6H_5, R″ = C_2H_5 or C_6H_5, and R‴ = C_6H_5.

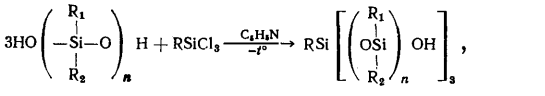
The X-ray diffraction studies, directed by Andrianov, on industrial and laboratory specimens of high-molecular-weight dialkyl(aryl)siloxane elastomers merit special consideration [68-73]. These investigations greatly amplified and extended the available data concerning the nature and physical properties of viscoelastic polydialkyl(aryl)siloxanes. The study of the effects of temperature, duration of exposure to a given temperature, deformation, the number and type of modifying groups, vulcanisation, and the amount and type of filler on the crystallisation processes of polydimethylsiloxanes (in the temperature range between −45° and −120°C) permitted a clear assessment of the influence of the above parameters on the process.

When modifying groups are introduced into the polymer, the rate and degree of crystallisation are described by relations with extrema [68,69]. The type of modifying groups does not have a significant influence on the crystallisation process. Vulcanisation [70] of polysiloxane elastomers affects the crystallisation processes like the introduction of modifying groups. The maximum rate of crystallisation is observed in the presence of an open vulcanisation network ($n \simeq 3000$). The introduction of a filler [71] accelerates the primary crystallisation process, because the filler orients on the surface the sections of the macromolecules which function as crystallisation nuclei. The rate of secondary crystallisation decreases with increase of the amount of filler and with increase of its activity. The crystallisation of deformed specimens proceeds via stages with an amorphous texture, the temperature of the onset of crystallisation being displaced towards higher values [72,73].

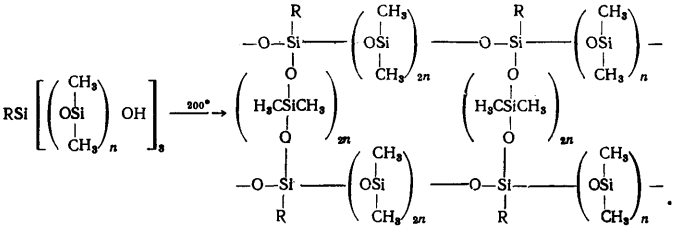
III. POLYMERS WITH CYCLONETWORK MOLECULAR STRUCTURES

The series of studies by Andrianov and coworkers described in this section was devoted to the investigation of a special class of polymeric compounds. This group of polymers is distinguished by a branched and partly cross-linked structure in which the siloxane bridges which behave as the cross-linking elements are polymeric. These compounds are obtained as a rule by polycondensation methods. Their synthesis makes it possible to regulate the distribution of the various groups or atoms in the polymer chain, which enables one to create polymers with a specified molecular structure and to regulate the properties of the polymers, whereas traditional hydrolytic polycondensation methods with subsequent catalytic polymerisation of the hydrolysis products as a rule lead to polymers with a non-order distribution of structural units.

The method of synthesising polyalkyl(aryl)siloxanes from polyfunctional oligomeric blocks is of interest for the preparation of polymers with an ordered structure [74-80]. Trifunctional alkyl(aryl)siloxane oligomers were synthesised in accordance with the scheme [81,82]

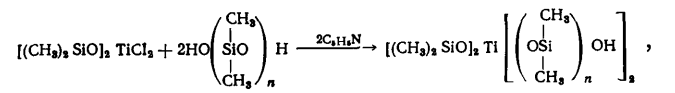


where R, R_1, and R_2 = CH_3 or C_6H_5 and n = 2, 6, 9, 14, or 32. The polycondensation of such oligomers leads to polymers with an ordered structure:

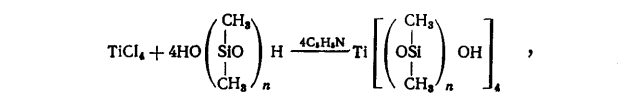


Polymers having this structure are thermoelastic and have satisfactory dielectric parameters [68]. The latter property is a consequence of the characteristic features of the method of synthesis of the polymers from oligomeric blocks. The polymers obtained by this procedure contain virtually no low-molecular-weight products and the polydispersity coefficient of the final product is low. The capacity of such polymers for crystallisation on cooling depends on the chain length between the cross-linking points. A polymer with a chain comprising 64 siloxane units crystallises in the temperature range between −67° and −72°C. When there are 18 siloxane units between the bridges, the polymer does not crystallise and passes to a vitreous state [68].

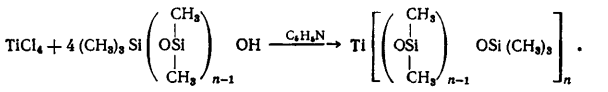
Compounds having a similar structure and containing polyfunctional metal atoms at the branching centres were obtained by heterofunctional condensation reactions. Titanodimethylsiloxane oligomers with linear and branched structures were obtained as follows [83-90]:



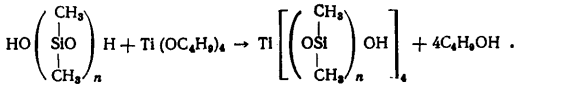
where n = 9, 22, 34, 42, and 52, and



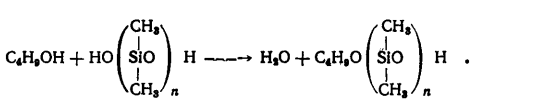
where n = 5, 13, 22, 25, 34, 42, 48, 52, 68, 80, or 104;



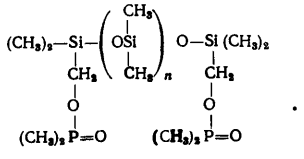
Compounds with this type of structure can also be obtained on the basis of tetrabutoxytitanium [90]:



The reaction proceeds in the above direction only when butanol is rapdily removed from the reaction sphere; otherwise the water formed in the reaction hydrolyses tetrabutoxytitanium to titanium dioxide:

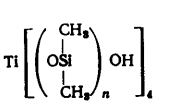


Oligomers having the above structure can react with the hydroxy-groups at the ends of the branches with formation of association complexes. As the concentration of hydroxy-groups increases (with decrease of the length from 34 dimethylsiloxane units to 13), they are gradually transformed from viscous liquids into gel-like substances. The above intermolecular interaction also leads to an increase of the packing density of the molecules. Similar features were likewise noted for polydimethylsiloxane oligomers with terminal dimethylphosphinate groups [85,86]:

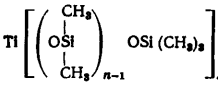


The activation energy for viscous flow, the density, and the refractive index increase with decrease of the distance between the terminal groups, which can be explained by the intensification of the interaction between the molecular chains with increase of the concentration of the polar groups per unit volume.

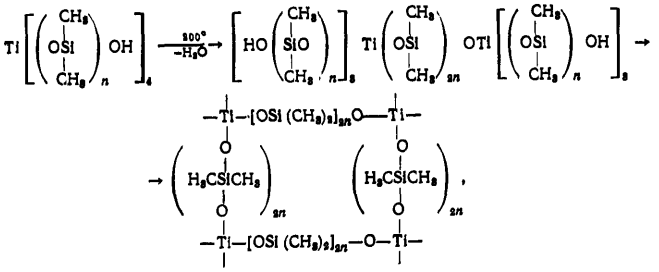
The variation of density with the length of the dimethylsiloxane chain for compounds of the type



is of a type opposite to that observed for the compounds [84]



The formation of polymers with a cyclonetwork structure [89] on condensation of branched oligomers proceeds in two stages via the formation of a soluble polymer:



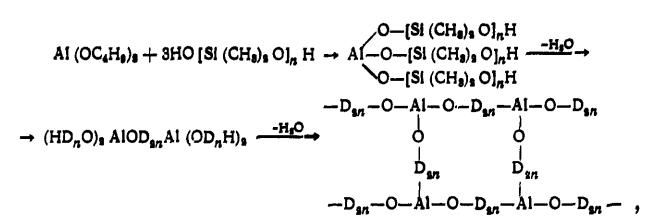
where n = 9, 18, 22, 25, 34, 42, 52, 62, 80. The structure formation reaction is first order and the structure formation rate constant decreases with increase of the average degree of polymerisation n in the initial oligomer. As the cyclonetwork structure develops in the polymer and solubility is lost, the polymer remains in the viscoelastic state up to 350°C.

X-Ray diffraction studies on these compounds showed [91] that they are amorphous at room temperature and their structure consists of packed bundles of dimethylsiloxane chains analogous to the packing of the molecular chains in polydimethylsiloxane. On cooling, the substances crystallise in the same temperature range as polydimethylsiloxane. It is interesting that, with increase of the hydroxy-group content in the compounds, the rigidity of the system rises, crystallisation is hindered, and the polarisability and dielectric losses increase [91].

A study of the thermal degradation of polytitanodimethylsiloxanes *in vacuo* showed [92] that degradation with rupture of the siloxane linkage and the formation of hexamethylcyclotrisiloxane is the rate-determining process. However, the introduction of a titanium atom into the siloxane chain appreciably reduces the rate of degradation. The rupture of the Si–O bond is accompanied by the homolytic rupture of the Si–C bond with liberation of hydrogen, methane, and ethane [93].

Compounds having a similar composition were obtained by the heterofunctional condensation of aluminium butoxide with difunctional oligomeric polyalkyl(aryl)siloxanes [94–97].

In this case the branching centre is the aluminium atom. The reaction proceeds in several stages:



where D designates the dimethylsiloxane unit $(CH_3)_2SiO$. A cross-linked polymer with a cyclonetwork structure is formed in the final stage of the process. The gel-formation rate constant depends little on the chain length of the initial oligomer, but amounts to 3.7×10^{-2}–1.4×10^{-2} h^{-1} when n for the oligomer ranges from 20 to 177 for a formally first order of the reaction with respect to the yield of the gel.

Thermal degradation of polymers of this type takes place in the temperature range 275–450°C. The main product is hexamethylcyclotrisiloxane and at 350°C methane and ethane are formed. The activation energy and the reaction order hardly depend on the distance between the nodes of the network. In this case the degradation process is a complex multistage reaction in which one can distinguish (a) thermal polycondensation in the initial stage, (b) random degradation of the polymer chain with formation of low-molecular-weight cyclic products, and (c) abstraction of organic groups from the silicon atom [92,93].

The polymers with a cyclonetwork structure examined in this section together with linear and branched polydimethylsiloxanes are convenient objects for the investigation of physicochemical properties.

A series of such studies greatly extended the existing knowledge of the nature of the siloxane chain in polymers having different structures [98–109]. An electron microscope study of polyalumino- and polytitano-dimethylsiloxanes showed that in both soluble and insoluble states these polymers have a two-stage globular supermolecular structure which is apparently of a type common to cross-linked viscoelastic polymers [98–101]. In the course of crystallisation the only structural form of polydimethylsiloxanes and polymetallodimethylsiloxanes comprises spherolytic formations. With increase of the distance between the metal atoms in the chain, the degree of crystallinity increases [102,103] together with the rate of crystallisation, which approaches the rate for high-molecular-weight polydimethylsiloxanes [100]. It is interesting that the above relation is much more pronounced for aluminium atoms at the nodes of the network than for titanium atoms.

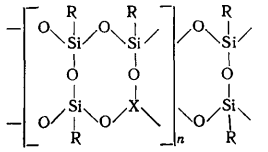
The somewhat specific character of the mechanical properties of the polymers (dependence of the modulus of elasticity, tensile strength, and deformation on n) is associated with the characteristics of the molecular and supermolecular structures [102,103]. The degree of structure formation in polyaluminodimethylsiloxanes can also be estimated by studying the relaxation properties. It was found that the increase of the equilibrium stress at the end of relaxation is faster for polymers with a low value of n. This conclusion agrees well with data obtained in a study of the kinetics of three-dimensional condensation and can be expressed by the relation $\lg \sigma_\infty = A - B \lg n$, where σ_∞ is the equilibrium stress at the end of relaxation, n the length of the siloxane chain between the nodal aluminium atoms, and A and B are constants characterising the given polymer.

The above relation makes it possible to investigate polymers in those cases where the lack of solubility precludes the investigation of the polymer structure by the usual methods [102,103].

IV. POLYMERS WITH CYCLOLINEAR LADDER MOLECULAR STRUCTURES

The possibility of the existence of polymeric molecules with a cyclolinear structure was first suggested by Andrianov together with one of the authors of the present review [104] and was subsequently confirmed by studies discussed in detail in a monograph [4]. Further investigations were directed towards finding new ways of synthesis and also to study the possibility of obtaining polymers having this structure, a high molecular weight, and different compositions of the elementary units. These compounds, which were subsequently called in the literature "ladder

polymers", have chain units with a silsesquioxane structure and can be represented by the general formula



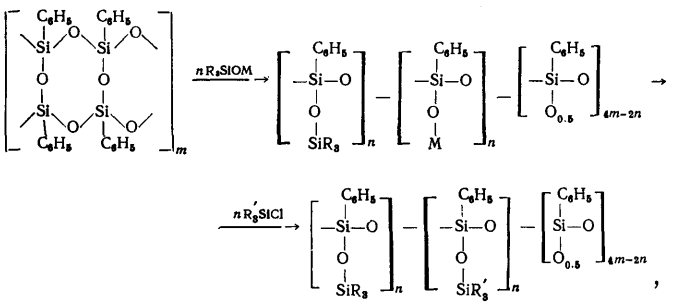
where X = Si, Al, Ti, Sn, etc.

A high-molecular-weight polyphenylsilsesquioxane, obtained initially by the high-temperature condensation of the hydrolysis product of trichlorophenylsilane [105], was subsequently obtained also by the polymerisation of a crystalline octamer [106] having the composition $(C_6H_5SiO_{4.5})_8$. In a series of tested polymerisation solvents (diphenyl ether, Dowtherm, nitrobenzene, anisole, and dimethylformamide) dimethylformamide proved to be best. In this case it is possible to obtain a polymer with a specific viscosity of 5.8. The polymer yields transparent films with a glass point above 400°C. The weight losses on heating to 500°C are 1.5–3.5% and not more than 15% at 600°C. The main polymer chain remains virtually unchanged up to 900°C. [107]

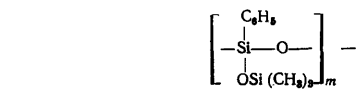
The specific structure of the molecule of the cyclolinear polyphenylsilsesquioxane in many respects determines its unusual physical properties. Thus the optical anisotropy of the molecules of this polymer exceeds by a factor of tens and hundreds the analogous parameters of the linear polymethylphenylsiloxane [108]. The number of monomer units per segment calculated from the experimental data is approximately 50, which exceeds by a factor of 10 the corresponding value for polymethylphenylsiloxane. This constitutes additional confirmation of the two-chain structure of the molecules of this ladder polymer. It is interesting that the high rigidity of the chain has little influence on the rotational mobility of the phenyl side groups [108]. It was noted that different specimens of the ladder polyphenylsiloxane have appreciably different molecular rigidities. This can be accounted for by the different proportions of structural defects in the molecules [109]. The nature of the flexibility of the ladder polymeric structure is different from that in linear polymers. It has a microdeformation mechanism (and not a rotational isomeric mechanism) involving microdistortions of the valence angles in the thermal vibrations of the atomic groups.

Appreciable differences between the structures of ladder polyphenylsiloxanes were also observed in a study of their hydrodynamic properties [110]. The values of the parameter a in Mark–Kuhn–Howink equation vary in the range 0.63–1.29.

The above investigations established that, regardless of the nature of the initial monomer, the synthesis of the polymers leads to two types of macromolecular structures. For each type of structure, there is a specific Mark–Kuhn–Howink equation. An electron microscope study on these two types of structures showed that they produce different supermolecular structures. Polymers with $a > 1$ give rise to structures of the fibrillar type and those with $a < 1$ give rise to globular structures. High values of the parameter a can be explained only by the high rigidity of the macromolecules, which causes appreciable deviations of the molecular coils from the Gaussian type even in the region of high molecular weights. The chemcal properties of the ladder polyphenylsilsesquioxane are determined by the high positive charge on the silicon atom and the negative inductive effect of the phenyl group, which increases the reactivity of the polymer in relation to nucleophilic agents. A polymer with a molecular weight of 30 000–40 000 was chosen for investigation. The reaction, carried out in accordance with the scheme

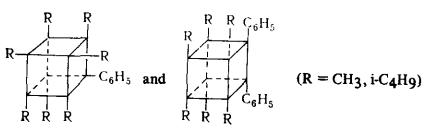


leads to oligomers with the above structure and a molecular weight of 1000–4000. [111,112] The ratio of units of different structure is statistical. Rearrangements of the siloxane skeletons with formation of six-membered structural fragments take place in the course of the above reaction together with the rupture of the silsesquioxane chain. The interaction of polyphenylsilsesquioxane with hexamethyldisiloxane at 250–260°C [113] leads to the formation of oligomers of the type



The analogous reaction with octamethylcyclotetrasiloxane [114] at 250°C leads to products with a viscosity smaller by a factor of 20 than that of the initial polyphenylsilsesquioxane.

A series of studies have been made on the synthetic possibilities and properties of ladder polymers containing, together with phenyl groups at the silicon atom, also groups with a different composition [115–129]. The synthesis and investigation of three-dimensional cyclic compounds of the type



(where each vertex contains a silicon atom and each edge represents a siloxane linkage) established that the introduction of electron-accepting phenyl substituents into the cage compounds is a necessary condition for their polymerisation, but is insufficient for their rearrangement to cyclolinear ladder polymers.

Cohydrolysis of a mixture of various alkyl(aryl)trichlorosilanes to compounds with a polycyclic structure and subsequent anionic polymerisation established a number of characteristics of the formation of the ladder structure [117,118]. An increase of the content of aliphatic substituents in the polycyclic systems decreases the rate of polymerisation. This effect is more pronounced the greater the length of the hydrocarbon chain of the alkyl substituents.

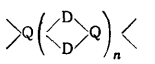
Compounds with alkyl substituents containing not more than three carbon atoms (regardless of the structure of the organic group) give rise to three-dimensional structures on polymerisation. The most favourable conditions for the formation of a ladder polymeric molecule arise when a double bond is introduced into the hydrocarbon chain of the substituent in the α-position relative to the silicon

atom. A similar effect is achieved when substituents are introduced into the phenyl group in the β-position relative to the silicon atom. The study of the hydrodynamic and dynamo-optical properties of the above polymers and of poly-3-methylbut-1-enylsilasesquioxane [123,124,129] made it possible to estimate the skeletal rigidity of the macromolecules. The thermomechanical and mechanical properties of these polymers [120,127] depend on the nature of the surrounding groups, the film-forming capacity being retained when the composition of the chain unit is altered. The thermal stability of ladder polymers greatly exceeds that of linear polyorganosiloxanes [121,126,127].

V. POLYMERS WITH SPIROCYCLIC AND SPIROLADDER MOLECULAR STRUCTURES

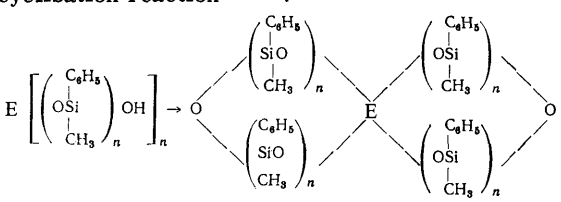
This class of polymers, which have an extremely unusual structure of the main molecular chains, opens a new chapter in the chemistry of organosilicon polymers, which has been developed very vigorously in recent years by Andrianov [128].

Polymers of this group contain cyclic fragments linked to the atom of an element forming part of two rings which constitute the molecular chain. The structure of a spirocyclic polymer can be represented schematically as follows:



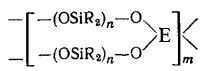
where D are bifunctional fragments and Q is the spirocyclic centre (a silicon or a polyvalent metal atom).

The possibility and ways of synthesising such polymers were predicted by earlier studies [137]. Thus it was noted that, when cross-like oligomers of type $E[(OSiR_2)nOH]_4$ are condensed, polymers with a molecular network structure are formed only when the distance between the central atom E and the functional group is large. The condensation of oligomers with small values of n leads to soluble polymers, which can be accounted for by an intramolecular cyclisation reaction [136,137]:



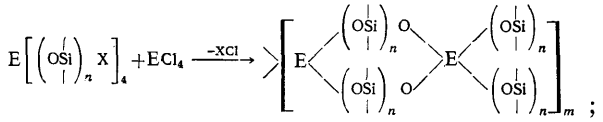
The compound with $n = 1$ is crystalline (E = Si), while those with $n = 3$ (E = Si or Ti) are amorphous under the usual conditions.

This reaction also involves the formation of a soluble polymer without hydroxy-groups. Thus the reaction proceeds simultaneously with intermolecular condensation and formation of polymers of the type

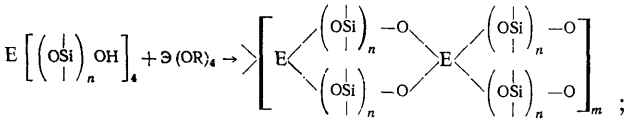


The following reactions have been used to synthesise spirocyclic polymers [128]:

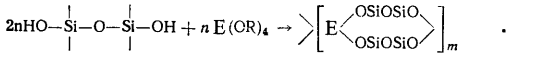
(1) exchange reactions:



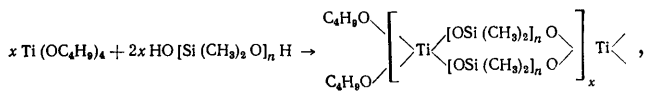
(2) polycondensation of tetrafunctional compounds:



(3) condensation of bifunctional compounds with tetrafunctional compounds:

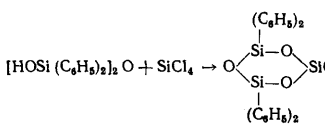


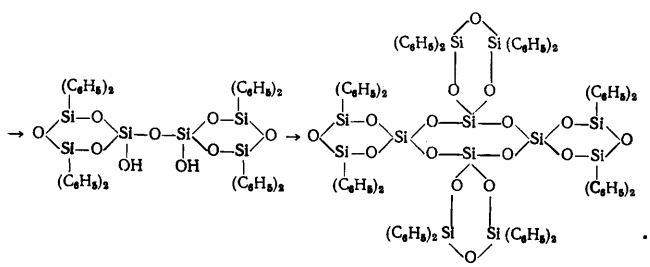
For example, polyspirotitanodimethylsiloxanes were obtained by the reaction [138]



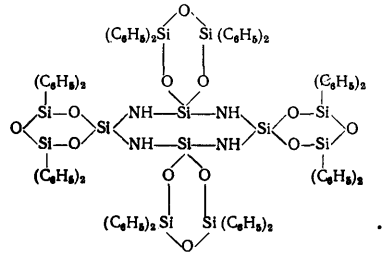
where $n = 2$, 3, or 4 and the molecular weight reaches 2000–3500. The low degree of polycondensation can be accounted for by the steric hindrance suffered by the reactant molecule on approaching the functional groups of the molecule of the polymer being formed. The spiro-structure of the resulting polymer is stable up to 300°C, [139] the spirocyclic fragments in the polymer molecules undergoing a rearrangement only at 400°C. Hydrodynamic and optical studies on these polymers [129] demonstrated the presence of a high degree of intramolecular order and a high equilibrium rigidity of the macromolecules.

One of the ways of obtaining polymers with a spirocyclic structure is catalytic polymerisation of organospirosiloxanes. The initial spiro-compounds were obtained by a multistage synthesis [130–133]:

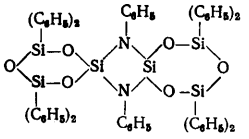




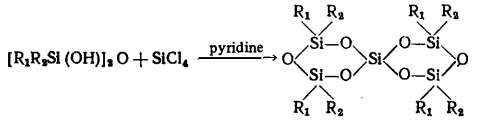
The last stage proceeds with difficulty and only at 280–300°C (owing to the screening effect of the diphenylcyclotrisiloxane fragments). The replacement of the second, hydrolytic stage in the above scheme by ammonolysis with ammonia makes it possible to obtain a silazane–siloxane spiro-compound:



On the other hand, when the ammonolysis is carried out with aniline, it is possible to obtain ultimately by the above scheme a spiro-compound with a four-membered silazane ring:

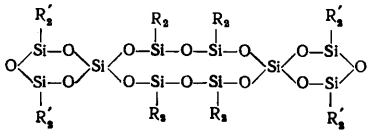


The above syntheses were achieved in the absence of a hydrogen chloride acceptor in the first stage. On the other hand, in the presence of pyridine, the spiro-compound is obtained in one stage:

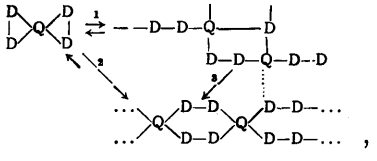


where R_1 and R_2 = CH_3 or C_6H_5.

In the course of high-temperature distillation these compounds partly rearrange to higher spirocyclic products:



It is interesting that the formation of cross-linked products is not observed. When organospirobicyclosiloxanes are subjected to anionic polymerisation in bulk [134,135], the growing polymer chain is involved in two competing reactions (intermolecular and intramolecular interactions). This can be represented by the scheme

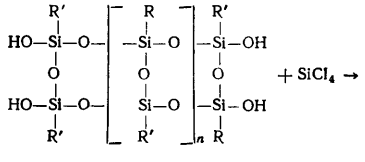


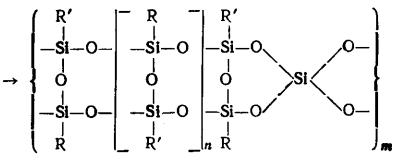
where D are bifunctional fragments and Q are tetrafunctional fragments.

The process proceeds both with formation of soluble (pathway 2) and cross-linked products (pathway 1). The content of the gel fraction falls as the surrounding methyl groups are replaced by phenyl groups. When the molecule of the initial compound contains exclusively phenyl groups, the gel is not formed.

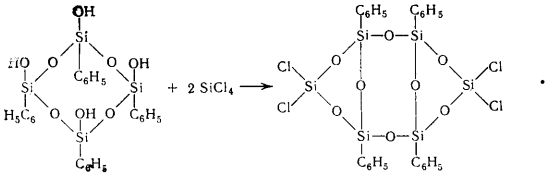
The polymerisation of the above compounds in dilute solutions [134] as a rule leads to the exhaustion of the initial cyclic fragments.

Compounds having polymer chains containing simultaneously fragments with spiro- and ladder structures constitute a special group of polymers. In their synthesis by heterofunctional condensation the most favourable conditions for the formation of the expected structure occur when the initial stage of the reaction proceeds at a low temperature in not too dilute solutions [140,141]:



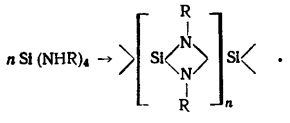


where R = C_6H_5, R′ = i-C_4H_9 or C_6H_5, and n = 0–2. The length of the cyclotetrasiloxane fragment (the value of n) affects the possibility of obtaining spiro-groups. For n = 2 and R = R′ = C_6H_5, it proved possible to obtain polymers with a characteristic viscosity of 0.12–0.22 dm g^{-1}, while for n = 0 the expected structures could not be produced. These results were explained by stepwise condensation:



The polycyclic compound formed has the *cis*-structure like the initial tetrol $[C_6H_5Si(OH)O]_4$. When the resulting polycyclic compound reacts with an equimolar amount of the tetrol, spiro-groups are not formed owing to the *cis*-conformation of the reactants.

The study of the hydrodynamic and optical properties of polyisobutylphenylsiloxane with a spiroladder structure [142] showed that the molecules have the properties of fairly flexible non-fluid coils, resembling Gaussian coils from the hydrodynamic standpoint. Such flexibility can be accounted for by structural defects. On the other hand, the behaviour of polymethylphenylspirosiloxane molecules (with 8 and 16 atoms in the ring) in solution differs from the usual behaviour of semirigid regular chains with both small and large segments, which can be explained from the standpoint of non-linear structures of the network type [141]. Spirocyclic polymers with a silazane structure [128] were synthesised by the reaction

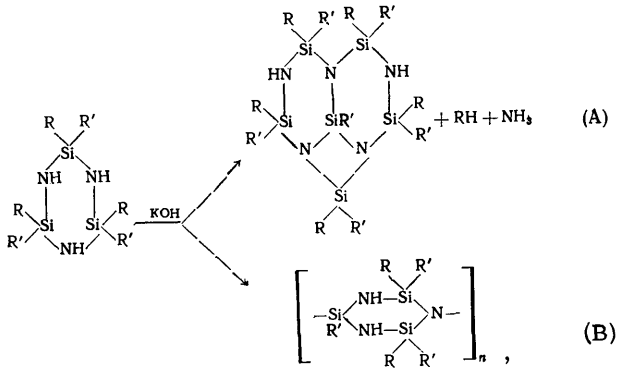


VI. POLYORGANOSILAZANES

Great hopes were associated with studies on polyorganosilazanes because there are many unsolved problems related to the synthesis, structures, and properties of organosilicon polymers, which could not be solved solely in relation to compounds of the siloxane series.

The reaction of organocyclosilaxanes with nucleophilic agents is the most promising from the standpoint of polymer chemistry. However, it differs appreciably from the analogous reaction of organocyclosiloxanes. In the first place, in contrast to organocyclosiloxanes, organocyclosilazanes exhibit a greater tendency to undergo substitution reactions than addition reactions. In this respect their properties resemble aromatic systems [142,143]. The reaction of dialkyl(aryl)cyclosilazanes with nucleophilic agents [144–154] is accompanied by the evolution of the hydrocarbon corresponding to the organic group attached to the silicon atom and the formation of cyclic polymers which soften at a high temperature. When the silicon

atom is surrounded by aliphatic groups, the reaction proceeds as follows:

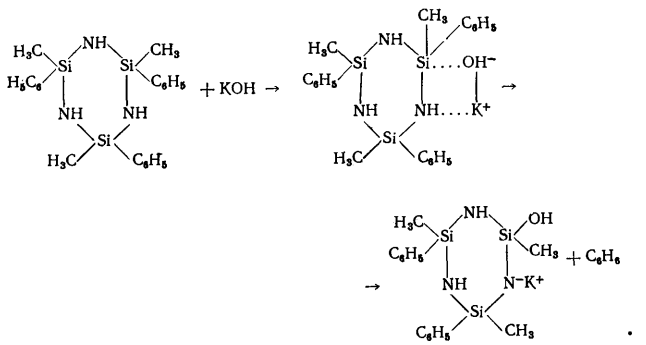


(A)

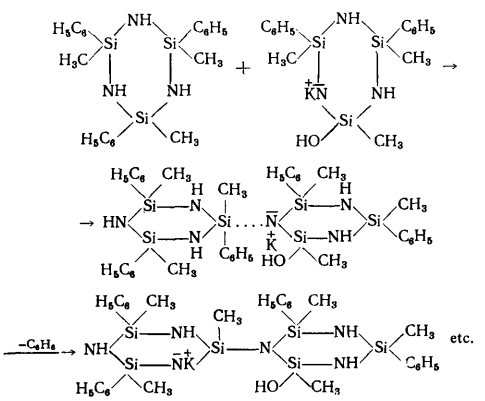
(B)

where R = CH_3 or C_2H_5 and R′ = C_2H_5, C_4H_9, or C_6H_{13}. It is interesting that compound (A) is chemically inert and remains unchanged when acted upon by catalytic amounts of alkali. The product (B) is formed via condensation without ring opening and not via compound (A).

The anionic polymerisation of methylphenylcyclosilazanes also does not proceed via ring opening, but involves the formation of a transition complex which weakens the Si–C bond and not the Si–N bond:



The subsequent reaction proceeds via the coordination of the molecules of the initial compound to the resulting anion, which contains the $\rangle N^-$ fragment:



The resulting polymers have a filamental or branched structure. An increase in the bulk of the organic group at the silicon atom stabilises the transition complex and hinders its conversion into the active state. As a result, the reaction rate falls sharply. The reaction involving trimethyltrinonylcyclotrisilazane does not begin up to 300°C. The influence of the groups surrounding the silicon atom is also associated with steric effects. Bulky groups (hexyl, octyl, and nonyl) hinder the polymerisation.

Studies on the possibility of synthesising polymers with silazoxane chains [155–159] revealed the fundamental pathways leading to the formation of polymers of this type. The synthesis of the polymers by the condensation method proved to be promising [157–159]:

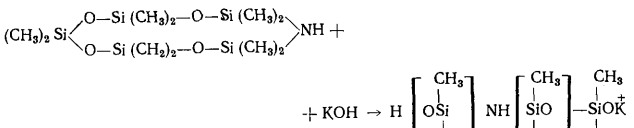
$$RN(H)[Si(CH_3)_2O]_n Si(CH_3)_2NHR \xrightarrow[-RNH_2]{t^\circ} \rightarrow R(H)N\{[Si(CH_3)_2O]_n Si(CH_3)_2NR\}_m H,$$

where R = H or C_2H_5 and $n = 4-10$, 11, or 40.

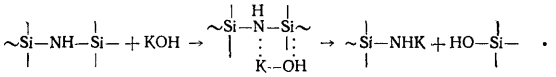
The polymers consist of swelling insoluble substances with a distinct region of a viscoelastic state. A study of the thermo-oxidative degradation of these polymers showed [160] that the introduction of a nitrogen atom into the siloxane chain stabilises it to some extent.

The anionic polymerisation of cyclosilazoxanes containing hydrogen at the nitrogen atom was unsuccessful.

The ring is opened initially at the siloxane linkages:

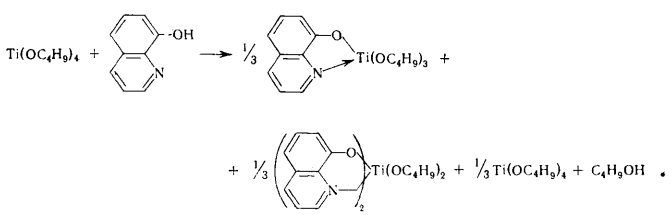


In the second reaction stage the polymeric chains are ruptured at the silazane linkages:

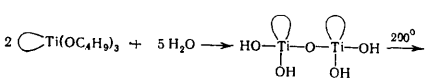


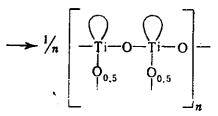
VII. POLYORGANOSILOXANE DERIVATIVES OF THE ELEMENTS

Polymers of this class were synthesised for the first time and investigated in detail by Andrianov's School. The main bulk of studies in this field have been described in a monograph [4]. Some of the investigations formally concerned with this field were examined in the preceding sections of the present review. This section deals with certain investigations published after the publication of Andrianov's monograph [4]. Numerous studies were devoted to polytitano-organosiloxanes. The replacement of one or two butoxy-groups in tetrabutoxytitanium by 8-hydroxyquinolinato-groups makes it possible to reduce the number of groups with which the titanium atom can interact to three and two respectively [161]:

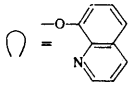


Hydrolysis of the tributoxy-compound with subsequent thermal condensation leads to polymers having a metalloxane structure [162]:

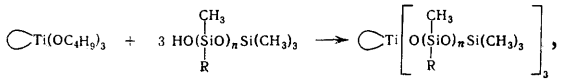




where



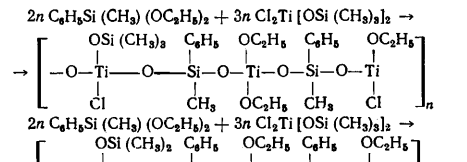
The reaction of the above trifunctional compound with hydroxylated polysiloxane oligomers leads to the formation of branched oligomers [163,164]:



where n = 15, 60, 98, 170, or 350 and R = CH_3 or C_6H_5.

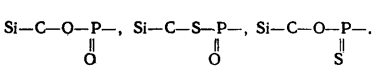
The resulting oligomers proved to be convenient model compounds for the study of the dependence of physicochemical properties on the siloxane chain length. It is interesting that the polydispersity coefficient of the oligomers does not differ significantly from that of the initial hydroxylated polyorganosiloxanes. The presence of 8-hydroxyquinolinatotitanoxane groups intensifies the intermolecular interaction and the packing density of the molecules, which affect the density, activation energy for viscous flow, and the free volume of the resulting oligomer [165]. An increase in the length of the siloxane chain in the branches has the opposite effect on the above parameters. The competing effects of various structural elements are observed particularly clearly in studies on the dynamic viscosity of oligomers. It has been established [164] that the introduction of 8-hydroxyquinolinatotitanoxane groups into polydimethylsiloxanes increases their thermal stability and the oligomers mentioned above are effective inhibitors of the thermo-oxidative degradation of liquid polydimethylsiloxanes.

Polymers with an unusual structure of the main chain, containing alternating titanium and silicon atoms, were obtained by heterofunctional condensation [166]:

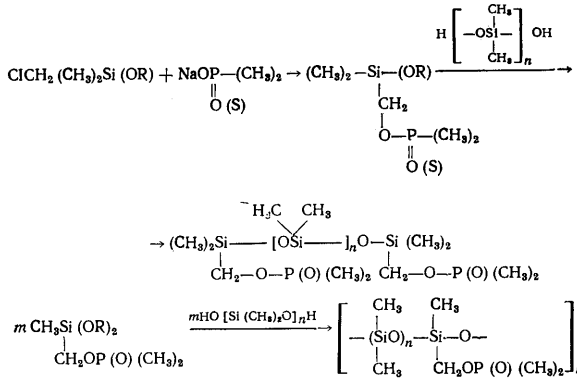


The resulting polymer is a viscoelastic product, which can be readily drawn into threads. Owing to the presence of hydrolysable groups the polymer is not resistant to moisture.

A number of studies have been made on the synthesis and properties of polyorganosiloxane polymers containing phosphorus atoms in the side chains [167-171]. In contrast to the majority of earlier studies on the nature of the Si–O–P linkage, the above series of investigations was devoted to compounds containing the groups

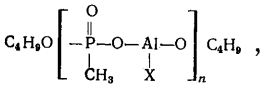


Such groups are much more resistant to hydrolysis than the Si–O–P group. Compounds of the siloxane series containing phosphinate groups or their thio-analogues in the methyl substituent at the silicon atom are synthesised by the reaction

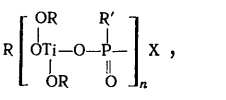


where n = 9, 13, 45, 75, or 130. By altering the proportions of the dimethylphosphinate and dimethylsiloxane groups, it is possible to vary the properties of the polymers within wide limits.

In this section of the review it is appropriate to mention studies dealing with methods for the synthesis of polymers with inorganic main molecular chains, without silicon atoms. These are primarily polyaluminomethylphosphonates [172-175]

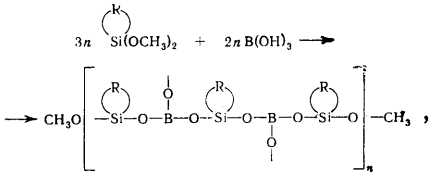


where X = Cl or C_4H_9, poly(dialkylphosphinyl)titanoxanes $\{[(CH_3)_2P(O)O_2TiO]\}_x$, [176,177] and polytitano-organophosphonates [178-180]

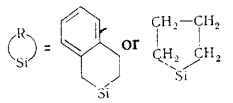


where R = C_4H_9, R′ = CH_3 or $CH_2{=}C(C_6H_5)$, and X = Cl, OH, or OC_2H_5. A detailed study of the properties of polytitano-organophosphinates established that their degradation at temperatures up to 400°C involves only the abstraction of the organic groups with retention of the Ti–O–P linkage [197,202]. It was established that these compounds can be used as thermostabilisers to improve the heat resistance of polyorganosiloxane varnishes and enamels [206]. The introduction of an organophosphinoxytitanoxane group into polyorganosiloxanes increases the resistance of the latter to thermo-oxidative degradation [202,203]. These results constituted the basis for the formation of siloxane resins with enhanced thermal stability [204,205].

Polyorganosiloxanes containing boron have been described [181-188]. Polymers with very variable compositions have been studied. Polyborosiloxanes containing silicon atoms in the main chain and at the same time silicon atoms behaving as the heteroelement in the heterocycle were obtained by the reaction

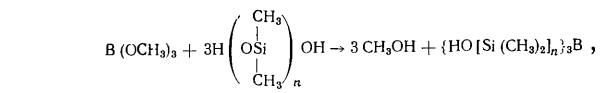


where

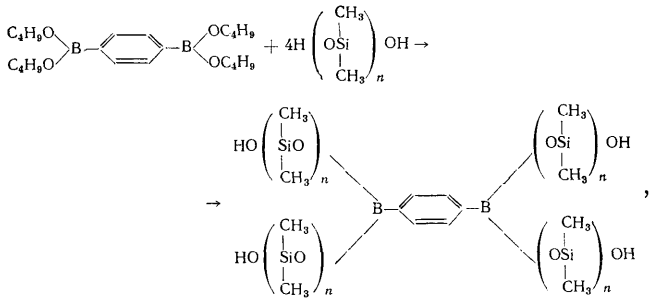


Polymers with this composition have a high resistance to thermo-oxidative degradation [186-188].

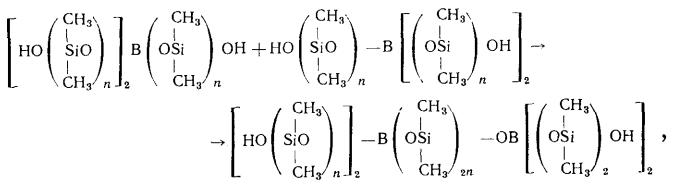
Branched polyborodimethylsiloxanes are synthesised by heterofunctional condensation [181-183]:



where n = 9, 13, 25, 45, 74, 135, or 220,

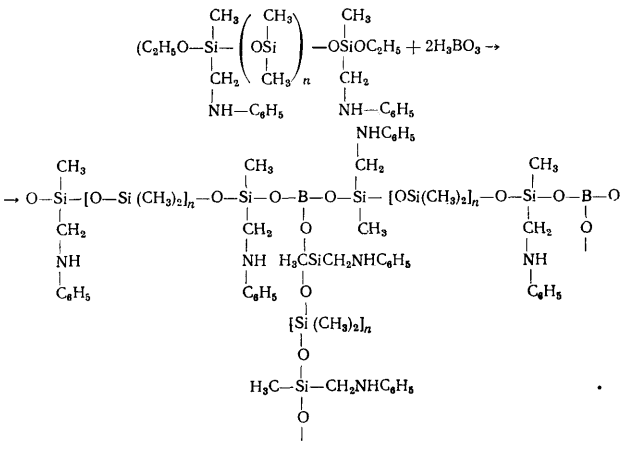


where n = 30, 46, 76, 95, or 235, and by homofunctional condensation [184,185]:



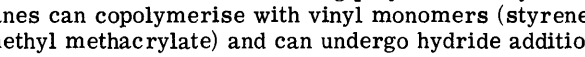
where n = 13, 25, 46, 74, or 200.

In the last of the polymers quoted the boron content is insignificant, and yet leads to an appreciable improvement of thermal stability compared with polydimethylsiloxanes [189]. The resistance of the SiOB linkage to hydrolysis was increased by the introduction of phenylaminomethyl groups among the organic substituents surrounding the silicon atom [183]:



The reason for the increased resistance to hydrolysis is in this case the formation of a coordinate bond between the nitrogen atom of the phenylaminomethyl group and the boron atom, which hinders the formation of a transition complex with water in the hydrolysis of these compounds.

A comparatively new development in the field of polymeric organosiloxane derivatives of the elements is the synthesis of polymetallo-organosiloxanes with reactive groups at the silicon atom, in particular vinyl groups [190-193]:



where M = Al or Ti. The resulting polymetallovinylsiloxanes can copolymerise with vinyl monomers (styrene and methyl methacrylate) and can undergo hydride addition reactions with compounds containing the SiH group. Both methods make it possible to vary widely the properties of the polymers both as a result of a change in the nature and amount of the metal introduced into the polymer and as a result of the selection of the appropriate vinyl monomer. The products of the addition of polytitanovinylsiloxanes to polyorganoaluminosiloxanes proved to be very effective components of heat-resistant adhesive compositions [193].

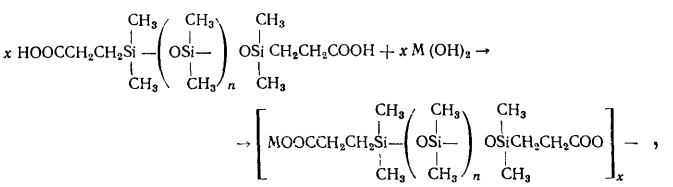
Polymeric organosiloxane derivatives of the elements constitutes a class of polymers differing from the majority of organic polymers, primarily by their high heat resistance. It is therefore quite natural that numerous studies have been devoted to the thermal and thermo-oxidative degradation of polymers of this class [189,194,201,207,208,209].

The above series of studies established the relation between the structure of the polymer unit, the nature of the heteroatom, the composition of the organic group at the silicon atom, and many other structural characteristics on the one hand and the thermal stability of the polymer on the other.

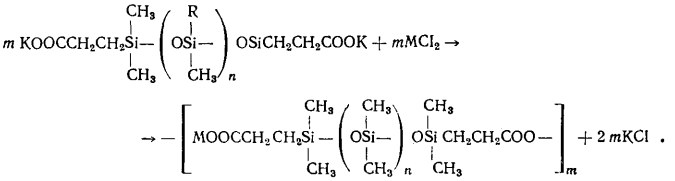
In conclusion of this section, we shall mention a number of studies on the synthesis and properties of polydimethylcarboxyatometalloxyloxanes containing metal atoms in the main chain linked to a silicon atom via a carboxylate group [212-222].

An attempt to introduce bivalent metal atoms into the siloxane chain was described in earlier investigations [210,211] and was found to involve many difficulties. A series of studies by Andrianov and coworkers [212,222] constitutes the most successful attempt at the introduction of bivalent metals into the siloxane chain, the carboxylate groups surrounding the metal atoms determining in many respects the unusual properties of these polymers.

The polymers were synthesised in two ways: (a) from the metal hydroxides:

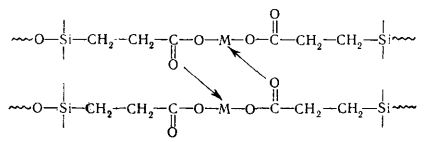


where M = Ca, Zn, Cd, Pb, or Co, and (b) from the metal chlorides:



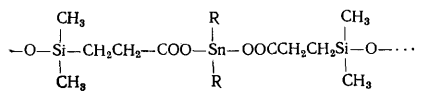
With increase of the distance between the metal atoms in the polymer chain, the viscosity of the polymer rises. Polymers with n = 20 are already rubber-like. Those with n = 50–70 are insoluble in the usual organic solvents

owing to the marked influence of interchain coordinate bonds of the type



The polymers become soluble when 2–3% of pyridine, which disturbs the above interactions, is introduced into the system. The presence of such linkages is also indicated by the high yield temperatures of the polymers and the high viscosities of the low-molecular-weight oligomer products of this type.

An additional confirmation of the presence of coordinate bonds in polymers of this kind has been provided by the study of a polymer based on quadrivalent tin, where such interactions are ruled out:



The properties of this polymer differ appreciably from those described above. Assuming the possibility of the formation of coordinate bonds between polymetallodimethylsiloxane macromolecules and their influence on the thermomechanical properties of the polymers, the metals investigated can be arranged in the following sequence in terms of decreasing intermolecular interaction forces due to these linkages [217,218]: Co > Zn > Pb,Ca > Cd.

This series agrees well with the order of decreasing coordination capacities of the metals. Studies on solutions of these polymers showed that, when the metal content is small (one atom for 30–100 silicon atoms), the conformation of the polymer molecule does not differ from that of the dimethylsiloxane polymers in solution [216]. It has also been established that the nature of the metal atom does not affect the rate of crystallisation of the polymers [218], but has an appreciable influence on the thermal degradation [222]. The thermal stability of the polymer increases with increasing basicity of the metal. These results together with those obtained by the chromatographic analysis of the thermal degradation products make it possible to elucidate the mechanism of the thermal decomposition of polymers of this type.

REFERENCES

1. K.A.Andrianov, USSR P.55 899; Byul.Izobret., No.10 (1939).
2. K.A.Andrianov, Zhur.Obshch.Khim., 8, 1255 (1938).
3. K.A.Andrianov, "Kremniiorganicheskie Soedineniya" (Organosilicon Compounds), GNTI Khim.Lit. SSSR, Moscow, 1955.
4. K.A.Andrianov, "Polimery s Neorganicheskimi Glavnymi Tsepyami Molekul" (Polymers with Inorganic Main Molecular Chains), Izd.Akad.Nauk SSSR, Moscow, 1962.
5. K.A.Andrianov, "Metody Elementoorganicheskoi Khimii. Kremnii" (Methods in the Chemistry of Organic Derivatives of the Elements. Silicon), Izd.Nauka, Moscow, 1968.
6. K.A.Andrianov, "Metalorganic Polymers", New York–London–Sydney, 1965.
7. K.A.Andrianov, "Kremniiorganicheskie Polimernye Soedineniya" (Polymeric Organosilicon Compounds), Gosenergoizdat, Moscow–Leningrad, 1946.
8. K.A.Andrianov and S.A.Yamanov, "Organicheskie Dielektriki i Ikh Primenenie v Promyshlennosti Sredstv Svyazi" (Organic Dielectrics and Their Applications in Communications Industry), Gosenergoizdat, Moscow–Leningrad, 1949.
9. K.A.Andrianov, "Kremniiorganicheskie Soedineniya v Tekhnike" (Organosilicon Compounds in Engineering), Izd.Znanie, Moscow, 1956.
10. K.A.Andrianov, "Kremniiorganicheskie Polimery v Narodnom Khozyaistve" (Organosilicon Polymers in the National Economy), Moscow, 1959.
11. K.A.Andrianov, "Khimiya Bol'shikh Molekul" (The Chemistry of Large Molecules), Moscow, 1961.
12. K.A.Andrianov, "Vysokomolekulyarnye Soedineniya v Narodnom Khozyaistve" (High-molecular-weight Compounds in the National Economy), Gosenergoizdat, 1961.
13. K.A.Andrianov and L.A.Epshtein, "Slyudinitovye Elektroizolyatsionnye Materialy" (Slyudinit Electroinsulating Materials) [Slyudinit = material derived from mica?], Gosenergoizdat, Moscow–Leningrad, 1963.
14. K.A.Andrianov and V.A.Skipetrov, "Sinteticheskie Zhidkie Dielektriki" (Synthetic Liquid Dielectrics), Moscow–Leningrad, 1962.
15. K.A.Andrianov, "Teplostoikie Kremniiorganicheskie Dielektriki" (Heat-resistant Organosilicon Dielectrics), Izd.Energiya, Moscow–Leningrad, 1964.
16. K.A.Andrianov and L.M.Khanashvili, "Tekhnologiya Elementoorganicheskikh Monomerov i Polimerov" (The Technology of Monomeric and Polymeric Organic Derivatives of the Elements), Izd.Khimiya, Moscow, 1973.
17. K.A.Andrianov and B.G.Zavin, USSR P.197 173; Byul.Izobret., No.12 (1967).
18. K.A.Andrianov and B.G.Zavin, Izv.Akad.Nauk SSSR, Neorg.Materialy, 2, 881 (1966).
19. K.A.Andrianov and B.G.Zavin, Izv.Akad.Nauk SSSR, Neorg.Materialy, 12, 2261 (1966).
20. K.A.Andrianov, B.G.Zavin, and N.V.Pertseva, Vysokomol.Soed., 10A, 46 (1968).
21. K.A.Andrianov, B.G.Zavin, S.A.Pavlova, and I.I.Tverdokhlebova, Vysokomol.Soed., 10B, 16 (1968).
22. K.A.Andrianov, N.V.Pertseva, and V.A.Temnikovskii, Vysokomol.Soed., 14A, 1816 (1972).
23. N.V.Pertseva, K.A.Andrianov, I.I.Tverdokhlebova, and S.A.Pavlova, Vysokomol.Soed., 12, 1001 (1970).
24. K.A.Andrianov, S.A.Pavlova, I.I.Tverdokhlebova, N.V.Pertseva, and I.V.Zhuravleva, Vysokomol.Soed., 13, 1727 (1971).
25. K.A.Andrianov, A.A.Zhdanov, A.M.Evdokimov, and B.G.Zavin, in "Vliyanie Vysshikh Atomnykh Orbitalei n Fizikicheskie i Khimicheskie Svoistva Soedinenii Neperekhodnykh Elementov" (Effect of the Highest Atomic Orbitals on the Physical and Chemical Properties of Compounds of Non-transition Elements), Izd.Zinatna, Riga, 1971, p.44.
26. K.A.Andrianov, A.A.Zhdanov, B.G.Zavin, and A.N.Evdokimov, Vysokomol.Soed., 13B, 397 (1971).
27. K.A.Andrianov, A.A.Zhdanov, B.G.Zavin, and A.N.Evdokimov, Dokl.Akad.Nauk SSSR, 199, 597 (1971).

28. K. A. Andrianov, B. G. Zavin, A. A. Zhdanov, A. M. Evdokimov, T. V. Biryukova, and B. D. Lavrukhin, Vysokomol. Soed., **14B**, 327 (1972).
29. K. A. Andrianov, A. A. Zhdanov, A. M. Edvokimov, L. A. Leites, and T. V. Biryukova, Dokl. Akad. Nauk SSSR, **206**, 866 (1972).
30. K. A. Andrianov, V. O. Reikhsfel'd, and A. M. Evdokimov, Izv. Akad. Nauk SSSR, Ser. Khim., 2358 (1972).
31. K. A. Andrianov and A. I. Petrashko, Vysokomol. Soed., **4**, 221 (1962).
32. K. A. Andrianov and A. I. Petrashko, Plast. Massy, No. 6, 17 (1964).
33. A. I. Petrashko, A. A. Zhdanov, and K. A. Andrianov, Izv. Akad. Nauk SSSR, Ser. Khim., 1276 (1964).
34. K. A. Andrianov, V. A. Temnikovskii, L. M. Khananashvili, B. G. Zavin, A. G. Kuznetsova, S. A. Golubtsov, and V. I. Ivanov, Vysokomol. Soed., **11B**, 637 (1969).
35. K. A. Andrianov, V. A. Temnikovskii, L. M. Khananashvili, and N. A. Lyapina, Dokl. Akad. Nauk SSSR, **189**, 311 (1969).
36. K. A. Andrianov, V. A. Temnikovskii, L. M. Khananashvili, and N. A. Lyapina, Vysokomol. Soed., **14A**, 2235 (1972).
37. K. A. Andrianov, S. A. Pavlova, I. I. Tverdokhlebova, N. V. Pertseva, and V. A. Temnikovskii, Vysokomol. Soed., **14A**, 1816 (1972).
38. K. A. Andrianov and M. A. Sipyagina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1392 (1962).
39. K. A. Andrianov, M. I. Klimova, L. N. Khananashvili, and M. A. Sipyagina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 651 (1963).
40. K. A. Andrianov, M. A. Sipyagina, and T. I. Fridshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 1672 (1963).
41. K. A. Andrianov and M. A. Sipyagina, Symposium, "Kremniiorganicheskie Soedineniya, Trudy Soveshchaniya" (Organosilicon Compounds. Conference Proceedings), Izv. NIITEKhIM, Moscow, 1967, No. III, p. 47.
42. K. A. Andrianov and M. A. Sipyagina, Vysokomol. Soed., **2**, 1113 (1966).
43. K. A. Andrianov, M. A. Sipyagina, L. S. Belova, and L. I. Kamenskaya, "Tezisy Dokladov Predstavlennykh na 4 Vsesoyuznoi Konferentsii po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii" (Abstracts of Reports Presented at the 4th All-Union Conference on the Chemistry and Applications of Organosilicon Compounds), Izd. NIITEKhIM, Moscow, 1968, p. 35.
44. K. A. Andrianov, V. M. Emel'yanov, and V. I. Troenko, "Tezisy Dokladov Predstavlennykh na 4 Vsesoyuznoi Konferentsii po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii" (Abstracts of Reports Presented at the 4th All-Union Conference on the Chemistry and Applications of Organosilicon Compounds), Izd. NIITEKhIM, Moscow, 1968, p. 71.
45. K. A. Andrianov, V. M. Emel'yanov, and V. I. Troenko, USSR P. 248 684; Byul. Izobret., No. 11 (1971).
46. K. A. Andrianov, V. M. Emel'yanov, and V. I. Troenko, Vysokomol. Soed., **12A**, 1718 (1970).
47. K. A. Andrianov, P. I. Zubov, L. A. Sukhareva, V. I. Emel'yanov, V. I. Troenko, Yu. P. Smirnova, and M. R. Kiselev, Dokl. Akad. Nauk SSSR, 197, 579 (1971).
48. K. A. Andrianov, T. V. Vasil'eva, V. I. D'yachenko, T. M. Karaseva, L. I. Makarova, and B. V. Molchanov, Zhur. Obshch. Khim., **43**, 768 (1973).
49. K. A. Andrianov, T. M. Karaseva, and L. I. Makarova, "Tezisy 18-i Konferentsii po Vysokomolekulyarnym Soedineniyam, Kazan" (Abstracts of the Reports and the 18th Conference on High-molecular-weight Compounds, Kazan), Izd. Nauka, Moscow, 1973, p. 192.
50. K. A. Andrianov and B. A. Izmailov, Izv. Akad. Nauk SSSR, Er. Khim., 1102 (1966).
51. K. A. Andrianov, B. A. Kochkin, B. Z. Izmailov, T. M. Karaseva, L. A. Sukhareva, and P. I. Zubov, Zhur. Obshch. Khim., 41, 1742 (1971).
52. B. A. Izmailov and K. A. Andrianov, "Novye Kremniiorganicheskie Soedineniya, Tezisy Dokladov" (New Organosilicon Compounds. Abstracts of Reports), 1966, p. 27.
53. M. B. Fromberg, Yu. K. Petrashko, and K. A. Andrianov, "Kremniiorganicheskie Soedineniya. Trudy Soveshchaniya" (Organosilicon Compounds. Conference Proceedings), Izd. NIITEKhIM, 1967, Moscow, No. 5, p. 56.
54. K. A. Andrianov, A. A. Zhdanov, and V. A. Odinets, Zhur. Obshch. Khim., **31**, 4033 (1961).
55. K. A. Andrianov, A. A. Zhdanov, and V. A. Odinets, Zhur. Obshch. Khim., **32**, 1126 (1962).
56. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, and I. V. Karpova, Dokl. Akad. Nauk SSSR, **162**, 335 (1965).
57. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, and I. V. Karpova, Zhur. Obshch. Khim., **36**, 521 (1966).
58. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, and I. V. Karpova, Izv. Akad. Nauk SSSR, Ser. Khim., 2733 (1969).
59. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, and I. V. Karpova, Izv. Akad. Nauk SSSR, Ser. Khim., 2238 (1971).
60. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, and I. V. Karpova, see Ref. 43, p. 75.
61. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, and I. V. Karpova, see Ref. 53, Vol. 3, p. 15.
62. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, and I. V. Karpova, Zhur. Obshch. Khim., 38, 627 (1968).
63. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, and I. V. Karpova, USSR P. 274 292; Byul. Izobret., No. 21 (1970).
64. K. A. Andrianov, A. I. Nogaideli, L. M. Khananashvili, and L. I. Nakaidze, Soobshch. Gruz. SSR, 48, 2, 323 (1967).
65. K. A. Andrianov, A. I. Nogaideli, L. M. Khananashvili, and L. I. Nakaidze, Izv. Akad. Nauk SSSR, Ser. Khim., 828 (1968).
66. K. A. Andrianov, A. I. Nogaideli, L. M. Khananashvili, and L. I. Nakaidze, Izv. Akad. Nauk SSSR, Ser. Khim., 2146 (1968).
67. L. I. Nakaidze, K. A. Andrianov, and A. I. Nogaideli, see Ref. 43, p. 77.
68. K. A. Andrianov, A. A. Zhdanov, Yu. K. Godovskii, V. Yu. Levin, D. Ya. Tsvankin, and V. A. Mosklenko, Vysokomol. Soed., 12A, 272 (1970).
69. K. A. Andrianov, G. L. Slonimskii, V. Yu. Levin, Yu. K. Godovskii, D. Ya. Tsvankin, V. A. Moskalenko, I. O. Kuznetsova, and L. I. Kuteinikova, Vysokomol. Soed., 12A, 240 (1970).
70. V. Yu. Levin, V. A. Koskalenko, A. A. Zhdanov, G. L. Slonimskii, K. A. Andrianov, D. L. Tsvankin, and F. A. Galil-Ogly, Vysokomol. Soed., 12A, 2588 (1970).

71. V. A. Moskalenko, V. Yu. Levin, A. A. Zhdanov, K. A. Andrianov, D. L. Tsvankin, G. L. Slonimskii, and F. A. Galil-Ogly, Vysokomol. Soed., 13A, 2685 (1971).
72. K. A. Andrianov, G. L. Slonimskii, A. A. Zdanov, V. Yu. Levin, Yu. K. Godowskii, and V. A. Moskalenko, J. Polymer Sci., 10, A1, 1 (1972).
73. K. A. Andrianov, G. L. Slonimskii, A. A. Zdanov, V. Yu. Levin, V. A. Moskalenko, and Yu. K. Godovskii, J. Polymer Sci., 10, A1, 23 (1972).
74. K. A. Andrianov, Dokl. Akad. Nauk SSSR, 140, 1310 (1961).
75. K. A. Andrianov, S. I. Dzhenchel'skaya, and Yu. K. Petrashko, Zhur. Obshch. Khim., 28, 685 (1958).
76. K. A. Andrianov, S. I. Dzhenchel'skaya, and Yu. K. Petrashko, "Trudy Konferentsii po Khimii i Prakticheskomu Preimeneniyu Kremniiorganicheskie Soedinenii, 1968" (Proceedings of the Conference on the Chemistry and Practical Applications of Organosilicon Compounds, 1968), TsBTI LSNKh, 1968, Vol. 1, No. 2, p. 45.
77. K. A. Andrianov, S. I. Dzhenchel'skaya, and Yu. K. Petrashko, Zhur. Prikl. Khim., 32, 1344 (1959).
78. K. A. Andrianov, S. I. Dzhenchel'skaya, and Yu. K. Petrashko, Plast. Massy, No. 3, 20 (1960).
79. K. A. Andrianov, M. B. Fromberg, and Yu. K. Petrashko, Zhur. Obshch. Khim., 33, 1448 (1963).
80. M. B. Fromberg, Yu. V. Petrashko, V. D. Vozhova, and K. A. Andrianov, Izv. Akad. Nauk SSSR, Ser. Khim., 660 (1965).
81. Yu. K. Petrashko, M. B. Fromberg, and K. A. Andrianov, Izv. Akad. Nauk SSSR, Ser. Khim., 1709 (1965).
82. Yu. K. Petrashko, M. B. Fromberg, V. I. Elinek, and K. A. Andrianov, see Ref. 53, p. 117.
83. K. A. Andrianov, N. A. Kurasheva, and N. V. Delazari, USSR P. 159 989; Byul. Izobret., No. 2 (1964).
84. K. A. Andrianov and N. A. Kurasheva, Izv. Akad. Nauk SSSR, Ser. Khim., 1976 (1965).
85. K. A. Andrianov, I. K. Kuznetsova, and M. I. Ermakova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 454 (1964).
86. K. A. Andrianov, I. K. Kuznetsova, and Yu. N. Smirnov, Izv. Akad. Nauk SSSR, Neorg. Materialy, 1, 289 (1965).
87. K. A. Andrianov and N. A. Kurasheva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1011 (1962).
88. K. A. Andrianov, N. A. Kurasheva, I. F. Manucharova, and E. M. Berliner, Izv. Akad. Nauk SSSR, Neorg. Materialy, 1, 294 (1965).
89. K. A. Andrianov, G. E. Golubkov, V. I. Elinek, N. A. Kurasheva, I. F. Manucharova, L. F. Litvinova, and B. I. Artem'ev, Vysokomol. Soed., 7, 680 (1965).
90. K. A. Andrianov, N. A. Kurasheva, and V. A. Avilov, Izv. Akad. Nauk SSSR, Ser. Khim., 1616 (1965).
91. K. A. Andrianov, G. E. Golubkov, V. I. Elinek, N. A. Kurasheva, I. F. Manucharova, L. F. Litvinova, and B. K. Artem'ev, Vysokomol. Soed., 7, 688 (1965).
92. K. A. Andrianov, A. A. Zhdanov, N. A. Kurasheva, G. L. Slonimskii, and V. S. Pankov, see Ref. 53, p. 33.
93. K. A. Andrianov, A. A. Zhdanov, V. V. Rode, N. A. Kurasheva, and M. A. Verkhotin, Vysokomol. Soed., 8, 1226 (1966).
94. K. A. Andrianov and A. A. Zhdanov, Dokl. Akad. Nauk SSSR, 138, 361 (1961).
95. K. A. Andrianov and A. A. Zhdanov, Izv. Akad. Nauk SSSR, Ser. Khim., 837 (1962).
96. K. A. Andrianov and A. A. Zhdanov, Vysokomol. Soed., 10A, 2102 (1968).
97. K. A. Andrianov and A. A. Zhdanov, J. Macromol. Sci., A2, No. 5, 963 (1968).
98. K. A. Andrianov, G. L. Slonimskii, A. I. Kitaigorodskii, A. A. Zhdanov, E. M. Belavtseva, and V. Yu. Levin, Dokl. Akad. Nauk SSSR, 166 (1966).
99. K. A. Andrianov, G. L. Slonimskii, A. A. Zhdanov, E. A. Katushina, and V. Yu. Levin, Vysokomol. Soed., 8, 5 (1966).
100. K. A. Andrianov, G. L. Slonimskii, A. A. Zhdanov, V. Yu. Levin, and N. L. Kurasheva, see Ref. 52, p. 73.
101. G. L. Slonimskii, K. A. Andrianov, A. A. Zhdanov, V. Yu. Levin, and E. M. Belavtseva, Vysokomol. Soed., 8, 1312 (1966).
102. G. L. Slonimskii, K. A. Andrianov, A. A. Zhdanov, and V. Yu. Levin, Vysokomol. Soed., 8, 11 (1966).
103. G. L. Slonimskii, K. A. Andrianov, A. A. Zhdanov, and V. Yu. Levin, Vysokomol. Soed., 9A, 1 (1967).
104. K. A. Andrianov and A. A. Zhdanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1033 (1954).
105. J. F. Brown, J. Polymer Sci., A1, 89 (1963).
106. K. A. Andrianov, G. A. Kurakov, F. F. Sushchentsova, V. A. Myagkov, and V. A. Avilov, Vysokomol. Soed., 7, 1477 (1965).
107. K. A. Andrianov, G. A. Kurakov, F. F. Sushchentsova, V. A. Myagkov, and V. A. Avilov, Dokl. Akad. Nauk SSSR, 166, 855 (1966).
108. V. N. Tsvetkov, K. A. Andrianov, E. L. Vinogradov, V. I. Pakhomov, and S. E. Yakushina, Vysokomol. Soed., 9A, 3 (1967).
109. V. N. Tsvetkov, K. A. Andrianov, G. I. Okhrimenko, M. G. Vitovskaya, V. I. Pakhomov, A. A. Yarosh, and D. N. Andreeva, Vysokomol. Soed., 12A, 1892 (1970).
110. K. A. Andrianov, S. A. Pavlova, I. I. Tverdokhlebova, V. I. Emel'yanova, T. A. Larina, and A. Yu. Rabkina, Vysokomol. Soed., 14A, 615 (1972).
111. K. A. Andrianov, V. S. Tikhonov, S. A. Tverskaya, V. I. Alanichev, and M. L. Chernobrovina, Zhur. Obshch. Khim., 40, 339 (1970).
112. V. S. Tikhonov, K. A. Andrianov, and S. A. Tverskaya, see Ref. 43, p. 83.
113. K. A. Andrianov, V. S. Tikhonov, and B. A. Astapov, Vysokomol. Soed., Kratkie Soobshch., 12, 577 (1970).
114. K. A. Andrianov, L. M. Khananashvili, and V. G. Zaval'nyi, Plast. Massy, No. 6, 48 (1967).
115. K. A. Andrianov and N. I. Makarova, Izv. Akad. Nauk SSSR, Ser. Khim., 1381 (1967).
116. K. A. Andrianov and N. I. Makarova, USSR P. 231 813; Byul. Izobret., No. 36 (1968).
117. K. A. Andrianov and N. I. Makarova, Izv. Akad. Nauk SSSR, Ser. Khim., 625 (1969).
118. K. A. Andrianov and N. I. Makarova, Vysokomol. Soed., 3A, 663 (1970).
119. K. A. Andrianov, G. L. Slonimskii, L. V. Genin, V. I. Gerasimov, D. L. Uvankin, V. Yu. Levin, and N. I. Makarova, Dokl. Akad. Nauk SSSR, 187, 1285 (1969).
120. K. A. Andrianov, G. L. Slonimskii, V. Yu. Levin, Yu. P. Kvachev, N. I. Makarova, and G. N. Kozlova, Vysokomol. Soed., 12B, 875 (1970).
121. K. A. Andrianov, G. L. Slonimskii, N. I. Makarova, I. A. Arkhipov, V. S. Papkov, and V. Yu. Levin, Vysokomol. Soed., 1B, 7 (1972).

122. V. I. Tsevtkov, K. A. Andrianov, M. G. Vitovskaya, N. I. Makarova, E. N. Zakharova, S. V. Bushin, and P. N. Lavrenko, Vysokomol. Soed., 2A, 311 (1972).
123. V. I. Tsvetkov, K. A. Andrianov, M. G. Vitovskaya, E. P. Astapenko, S. V. Bushchin, V. M. Yamshchikov, and N. I. Makarova, Vysokomol. Soed., 15A, 2549 (1973).
124. V. I. Tsvetkov, K. A. Andrianov, M. G. Vitovskaya, S. V. Bushchin, E. N. Zakharova, A. A. Gorbunov, P. N. Lavrenko, and N. I. Makarova, Vysokomol. Soed., 15A, 872 (1973).
125. K. A. Andrianov, G. L. Slonimskii, V. Yu. Levin, E. M. Belavtseva, N. I. Makarova, E. E. Obolonkova, and Yu. P. Kvachev, Vysokomol. Soed., 15B, 395 (1975).
126. K. A. Andrianov, G. L. Slonimskii, D. L. Tsvankin, V. S. Papkov, V. Yu. Levin, Yu. P. Kvachev, N. I. Makarova, and M. I. Il'ina, Vysokomol. Soed., 16B, 208 (1973).
127. K. A. Andrianov, A. A. Zhdanova, G. L. Slonimskii, V. Yu. Levin, V. S. Papkov, N. I. Makarova, and Yu. P. Kvachev, Dokl. Akad. Nauk SSSR, 215, 1373 (1974).
128. K. A. Andrianov, Dokl. Akad. Nauk SSSR, 191, 347 (1970).
129. V. N. Tsvetkov, K. A. Andrianov, E. I. Ryumtsev, I. N. Shtennikova, M. G. Vitovskaya, N. I. Makarova, and N. A. Kurasheva, Vysokomol. Soed., 15A, 400 (1973).
130. K. A. Andrianov, A. B. Zachernyuk, and S. A. Danielov, Khim. Geterotsikl. Soed., 893 (1972).
131. K. A. Andrianov and A. B. Zachernyuk, Khim. Geterotsikl. Soed., 1183 (1972).
132. K. A. Andrianov, A. B. Zachernyuk, and B. D. Lavrukin, Dokl. Akad. Nauk SSSR, 207, 593 (1972).
133. K. A. Andrianov, A. B. Zachernyuk, B. D. Lavrukhin, and N. G. Vasilenko, Dokl. Akad. Nauk SSSR, 204, 1112 (1972).
134. A. B. Zachernyuk and K. A. Andrianov, "Tezisy XVIII Konferentsii po Vysokomolekulyarnym Soedineniyam, g. Kazan', 1973" (Abstracts of Reports at the 18th Conference on High-molecular-weight Compounds, Kazan, 1973), p. 191.
135. K. A. Andrianov and A. B. Zachernyuk, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 19, 107 (1974).
136. N. P. Gashnikova, K. A. Andrianov, and M. A. Sipyagina, see Ref. 43, p. 35.
137. K. A. Andrianov, M. A. Sipyagina, and N. P. Gashnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 2493 (1970).
138. K. A. Andrianov, N. A. Kurasheva, B. D. Lavrukhin, and L. I. Kuteinikova, Vysokomol. Soed., 14A, 2450 (1972).
139. K. A. Andrianov, N. A. Kurasheva, L. I. Kuteinikova, and I. V. Zhuravleva, Vysokomol. Soed., 15A, 832 (1973).
140. K. A. Andrianov and N. I. Makarova, USSR P. 326 198; Byul. Izobret., No. 4 (1972).
141. K. A. Andrianov, V. I. Tsvetkov, M. G. Vitovskaya, N. I. Makarova, P. N. Lavrenko, T. I. Garmonova, E. P. Astapenko, and S. B. Bushin, Vysokomol. Soed., 12A, 2746 (1971).
142. K. A. Andrianov, Vysokomol. Soed., 11A, 1362 (1969).
143. K. A. Andrianov, Vysokomol. Soed., 13A, 253 (1971).
144. K. A. Andrianov and G. L. Rumba, Vysokomol. Soed., 4, 1010 (1962).
145. K. A. Andrianov and G. V. Kotrelev, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 472 (1966).
146. K. A. Andrianov and G. V. Kotrelev, Vysokomol. Soed., 4, 691 (1964).
147. K. A. Andrianov, G. V. Kotrelev, and V. M. Kotov, Zhur. Obshch. Khim., 35, 2176 (1965).
148. K. A. Andrianov and G. V. Kotrelev, Khim. Geterotsikl. Soed., 145 (1967).
149. K. A. Andrianov, G. D. Kotrelev, D. B. Levrukin, and L. N. Orobinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2275 (1967).
150. K. A. Andrianov, G. V. Kotrelev, and L. O. Kogan, Khim. Geterotsikl. Soed., 364 (1967).
151. K. A. Andrianov and G. V. Kotrelev, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1158 (1967).
152. K. A. Andrianov, V. P. Bazov, and G. B. Kotrelev, Dokl. Akad. Nauk SSSR, 176, 579 (1967).
153. K. A. Andrianov and G. V. Kotrelev, J. Organomet. Chem., 7, 217 (1967).
154. K. A. Andrianov, G. V. Kotrelev, B. A. Kamaritsky, J. H. Unitsky, and N. J. Sidorova, J. Organomet. Chem., 16, 51 (1969).
155. K. A. Andrianov, L. M. Volkova, and V. N. Talanov, Izv. Akad. Nauk SSSR, Ser. Khim., 2045 (1963).
156. K. A. Andrianov, V. N. Talanov, L. M. Khananashvili, and E. S. Sobolev, Izv. Akad. Nauk SSSR, Neorg. Materialy, 1, 1849 (1965).
157. K. A. Andrianov, K. N. Talanov, L. M. Khananashvili, Yu. Gelei, and N. P. Gashnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 2546 (1967).
158. K. A. Andrianov, V. N. Talanov, L. M. Khananashvili, T. V. Minakova, and N. P. Gashnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 661 (1968).
159. K. A. Andrianov, V. N. Talanov, L. M. Khananashvili, and T. G. Borodchenkova, Izv. Akad. Nauk SSSR, Ser. Khim., 2004 (1969).
160. K. A. Andrianov, A. G. Kolchina, N. V. Varlamova, V. N. Talanov, and S. E. Yakushkina, Izv. Akad. Nauk SSSR, Ser. Khim., 361 (1968).
161. K. A. Andrianov, Sh. V. Pichkhadze, V. M. Novikov, and I. L. Lavygin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2138 (1962).
162. K. A. Andrianov and I. A. Lavygin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1857 (1963).
163. K. A. Andrianov, I. A. Lavygin, and Yu. A. Shvetsov, Zhur. Obshch. Khim., 25, 689 (1965).
164. K. A. Andrianov, I. A. Lavygin, G. S. Tubyanskaya, R. I. Kobzova, and E. M. Oparina, Khim. i Tekhnol. Topliv i Masel, No. 5, 43 (1965).
165. K. A. Andrianov and I. A. Lavygin, Vysokomol. Soed., 7, 680 (1965).
166. K. A. Andrianov and N. A. Kurasheva, Dokl. Akad. Nauk SSSR, 135, 316 (1960).
167. K. A. Andrianov and I. K. Kuznetsova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1454 (1961).
168. K. A. Andrianov and I. K. Kuznetsova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1792 (1961).
169. K. A. Andrianov, I. K. Kuznetsova, N. A. Kurasheva, and E. I. Gerkhardt, Dokl. Akad. Nauk SSSR, 140, 365 (1961).
170. K. A. Andrianov and I. K. Kuznetsova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 456 (1962).
171. K. A. Andrianov, I. K. Kuznetsova, and I. E. Pakhomova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 500 (1963).
172. K. A. Andrianov, A. A. Zhdanov, and A. A. Kazakova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 465 (1959).

173. K.A.Andrianov, A.A.Zhdanov, and A.A.Kazakova, Zhur.Obshch.Khim., 29, 1281 (1959).
174. K.A.Andrianov, A.A.Zhdanov, L.M.Khananashvili, and A.S.Shapatin, Zhur.Obshch.Khim., 31, 224 (1961).
175. K.A.Andrianov, A.A.Zhdanov, A.A.Kazakova, and T.F.Baksheeva, Vysokomol.Soed., 6, 940 (1964).
176. K.A.Andrianov and I.K.Kuznetsova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 651 (1964).
177. K.A.Andrianov and I.K.Kuznetsova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 945 (1965).
178. K.A.Andrianov, I.K.Kuznetsova, and N.P.Gashnikova, Izv.Akad.Nauk SSSR, Neorg. Materialy, 1, 460 (1965).
179. K.A.Andrianov, I.K.Kuznetsova, and Yu.N.Smirnov, Izv.Akad.Nauk SSSR, Neorg.Materialy, 1, 301 (1965).
180. K.A.Andrianov, I.K.Kuznetsova, T.Bebchuk, A.Kolchina, and I.Shaipova, Izv.Akad.Nauk SSSR, Neorg.Materialy, 1, 517 (1965).
181. K.A.Andrianov and M.N.Ermakova, Zhur.Obshch. Khim., 31, 1310 (1961).
182. K.A.Andrianov and M.N.Ermakova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1577 (1962).
183. K.A.Andrianov and M.N.Ermakova, Izv.Akad.Nauk SSSR, Neorg.Materialy, 1, 825 (1965).
184. K.A.Andrianov, M.N.Ermakova, and G.F.Sablina, Vysokomol.Soed., 7, 1771 (1965).
185. K.A.Andrianov and M.N.Ermakova, Izv.Akad.Nauk SSSR, Ser.Khim., 680 (1966).
186. K.A.Andrianov and M.N.Ermakova, Izv.Akad.Nauk SSSR, Ser.Khim., 896 (1968).
187. K.A.Andrianov, M.N.Ermakova, and O.K.Ostapenko, Izv.Akad.Nauk SSSR, Ser.Khim., 2007 (1968).
188. K.A.Andrianov, M.N.Ermakova, T.Szekely, and G.Garzo, Vysokomol.Soed., 2A, 164 (1969).
189. K.A.Andrianov, M.A.Verkhotin, M.N.Ermakova, S.R.Rafikov, and V.V.Rode, Vysokomol.Soed., 8, 2139 (1966).
190. A.A.Zhdanov, K.A.Andrianov, G.A.Fetisov, and L.A.Leites, Zhur.Obshch.Khim., 37, 2311 (1967).
191. A.A.Zhdanov, K.A.Andrianov, G.A.Fetisov, and L.M.Isaeva, Vysokomol.Soed., 9A, 2620 (1967).
192. A.A.Zhdanov, K.A.Andrianov, and G.A.Fetisov, Vysokomol.Soed., 11A, 477 (1969).
193. A.A.Zhdanov, K.A.Andrianov, and G.A.Fetisov, USSR P.223 336; Byul.Izobret., No.24 (1968).
194. S.R.Rafikov, M.A.Verkhotin, V.V.Rode, and K.A.Andrianov, Dokl.Akad.Nauk SSSR, 171, 1352 (1966).
195. A.A.Zhdanov, K.A.Andrianov, and M.M.Levitskii, Vysokomol.Soed., 12, 551 (1970).
196. I.M.Kolesnikov, G.M.Panchenkov, K.A.Andrianov, A.A.Zhdanov, N.N.Belov, and M.M.Levitskii, Izv.Akad.Nauk SSSR, Ser.Khim., 488 (1974).
197. K.A.Andrianov, A.G.Kolchina, N.V.Varlamova, M.F.Borisov, and N.G.Grebenshchikova, Plast. Massy, No.3, 33 (1966).
198. K.A.Andrianov, A.G.Kolchina, I.K.Kuznetsova, and T.F.Bebchuk, Izv.Akad.Nauk SSSR, Neorg. Materialy, 2, 1913 (1966).
199. K.A.Andrianov, A.G.Kolchina, S.E.Yakushkina, N.V.Varlamova, and V.N.Talanov, Izv.Akad.Nauk SSSR, Ser.Khim., 361 (1968).
200. K.A.Andrianov, A.G.Kolchina, V.V.Severnyi, N.V.Varlamova, and A.S.Shapatin, Zhur.Obshch. Khim., 40, 1560 (1970).
201. K.A.Andrianov, A.G.Kolchina, N.A.Sipyagina, T.S.Bebchuk, and V.L.Kovalenko, Izv.Akad.Nauk SSSR, Ser.Khim., 1318 (1972).
202. N.V.Varlamova, V.V.Severnyi, K.A.Andrianov, A.G.Kolchina, and N.F.Vishnevskii, see Ref.53, p.86.
203. N.V.Varlamova, A.I.Sidnev, V.V.Severnyi, K.A.Andrianov, and I.A.Zubkov, see Ref.43, p.89.
204. A.S.Sergeev, K.A.Andrianov, I.T.Gridunov, L.M.Khananashvili, N.V.Varlamova, and L.Z.Khazen, see Ref.43, p.177.
205. K.A.Andrianov, A.S.Sergeev, L.M.Khananashvili, I.T.Gridunov, A.S.Shapatin, N.V.Varlamova, and A.V.Varlamov, Kauchuk i Rezina, No.7, 11 (1969).
206. V.V.Severnyi, N.V.Varlamova, K.A.Andrianov, A.A.Zaitseva, T.F.Altukhova, and A.S.Shapatin, Lakokrasochnye Materialy, No.3, 33 (1970).
207. V.S.Papkov, G.L.Slonimskii, K.A.Andrianov, A.A.Zhdanov, and E.S.Yakushkina, see Ref.43, p.123.
208. K.A.Andrianov, A.A.Zhdanov, N.A.Kurasheva, G.L.Slonimskii, and V.S.Papkov, see Ref.53, p.33.
209. K.A.Andrianov, E.Z.Asnovich, T.S.Bebchuk, M.A.Golubenko, and A.B.Lyakhova, see Ref. 53, p.98.
210. K.A.Andrianov and A.A.Zhdanov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1590 (1959).
211. K.A.Andrianov and A.A.Zhdanov, see Ref.76, p.100.
212. K.A.Andrianov, A.A.Zhdanov, and E.A.Kashutina, Zhur.Obshch.Khim., 32, 297 (1962).
213. K.A.Andrianov, A.A.Zhdanov, and E.A.Kashutina, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 454 (1962).
214. K.A.Andrianov, A.A.Zhdanov, and E.A.Kashutina, Zhur.Obshch.Khim., 35, 1037 (1965).
215. A.A.Zhdanov, K.A.Andrianov, and E.A.Kashutina, Dokl.Akad.Nauk SSSR, 171, 103 (1966).
216. A.A.Zhdanov, K.A.Andrianov, E.A.Kashutina, and A.N.Kulichkina, Vysokomol.Soed., 9, 373 (1967).
217. K.A.Andrianov, G.L.Slonimskii, A.A.Zhdanov, E.A.Kashutina, V.Yu.Levin, and E.A.Volkova, Vysokomol.Soed., 12A, 2690 (1970).
218. K.A.Andrianov, A.A.Zhdanov, G.L.Slonimskii, E.A.Kashutina, and V.Yu.Levin, Vysokomol.Soed., 8, 898 (1966).
219. A.A.Zhdanov, E.A.Kashutina, and A.A.Andrianov, see Ref.53, p.73.
220. E.A.Kashutina, K.A.Andrianov, and A.A.Zhdanov, see Ref.43, p.103.
221. K.A.Andrianov, A.A.Zhdanov, and E.A.Kashutina, USSR P.176 066; Byul.Izobret., No.21 (1965).
222. T.Szekely, G.Garzo, K.A.Andrianov, A.A.Zhdanov, and E.A.Kashutina, Vysokomol.Soed., 14A, 2497 (1972).

Institute of Organic
Derivatives of the
Elements, USSR
Academy of Sciences,
Moscow