U. D. C. 547.1'128

Methods of Synthesis of αω-Difunctional Oligosiloxanes with Two Organic Substituents Per Unit

M.G.Voronkov and N.G.Sviridova

The methods of preparation of oligosiloxanes with two organic substituents per unit, containing the functional groups $X(R_2SiO)_nSiR_2X$ (X = Cl, OCOR, OR, NR_2, OH, or ONa) at the terminal silicon atom, have been considered and a critical assessment of the possibility of employing the methods for the synthesis of oligomers with specified n and X has been made.
The bibliography includes 187 references.

CONTENTS

I.	Introduction	819
II.	Methods of synthesis of αω-dihalogeno-oligosiloxanes	819
III.	Methods of synthesis of αω-diacyloxyoligosiloxanes	823
IV.	Methods of synthesis of αω-dialkoxyoligosiloxanes	825
V.	Methods of synthesis of αω-diamino-oligosiloxanes	827
VI.	Synthesis of oligosiloxane-αω-diols	828
VII.	Preparation of disodium salts of oligosiloxane-αω-diols	831

I. INTRODUCTION

Recently organosilicon oligomers containing reactive substituents at the ends of the chain have assumed increasing theoretical and practical interest. These compounds occupy an intermediate position between organosilicon monomers and polymers, which have been thoroughly investigated and widely described in the chemical literature.

The most important application of αω-difunctional organosilicon oligomers is the synthesis of polymers with regular structures. By controlling the sequence of fragments in the main chains of the macromolecules, it is possible to alter sharply the properties of the polymers without affecting or only slightly altering their composition. Condensation of αω-difunctional oligomers with organic and inorganic monomers, organic derivatives of the elements, and also with one another makes it possible to obtain new types of polymers with valuable technical properties. This reaction has already found wide application in the synthesis of organosilicon block polymers, siloxanes with a number of atoms of other elements, and other types of silicon-containing high-molecular-weight compounds.

Organosilicon oligomers can also be used themselves as heat exchangers, stabilisers for rubber mixtures based on organosilicon polymers, etc.

The methods of preparation of αω-difunctional organosilicon oligomers have not so far been adequately treated in monographs on organosilicon chemistry and in reviews. The aim of the present paper is to fill this gap. It deals with the methods of synthesis of αω-difunctional oligosiloxanes which can be isolated in a pure form.

II. METHODS OF SYNTHESIS OF αω-DIHALOGENO-OLIGOSILOXANES

1. Partial Hydrolysis of Chlorosilanes with an Organic Substituent

Hydrolysis of chlorosilanes with an organic substituent is one of the most important reactions in organosilicon chemistry. This reaction makes it possible to convert such chlorosilanes, obtained by direct synthesis from silicon and halogeno-derivatives of hydrocarbons[1-5], directly into siloxane polymers with organic substituents.

Hydrolysis of dichlorosilanes with two organic substituents by an excess of water usually leads to the formation of cyclosiloxanes and only an insignificant amount of linear siloxanes[6-8]. In the presence of a deficiency of water, the principal hydrolysis products are linear oligosiloxanes with chlorine atoms at the ends of the chain. As a rule, hydrolysis yields a mixture of oligomers with various contents of silicon atoms in the molecule:

$$n\,RR'SiCl_2 + (n-1)\,H_2O \rightarrow Cl(RR'SiO)_{n-1}SiRR'Cl + 2(n-1)\,HCl,$$

where $n \geqslant 2$. The hydrolysis is usually carried out in a solvent, sometimes in the presence of a hydrogen chloride acceptor.

Thus αω-dichloro-oligodimethylsiloxanes with the general formula $Cl[(CH_3)_2SiO]_{n-1}Si(CH_3)_2Cl$ are obtained in the hydrolysis of dichlorodimethylsilane with water, the reactants being in molar proportions of 2:1.[9,10] The maximum yields of these oligomers (28% for $n = 2$, 24% for $n = 3$, 15% for $n = 4$, 6% for $n = 5$, 3% for $n = 6$, and 2% for $n > 6$) can be achieved by hydrolysis in a homogeneous medium using a mixture of ether and dioxane as a solvent. Under these conditions, 22% of the initial $(CH_3)_2SiCl_2$ does not react.

In hydrolysis in the absence of a solvent (a two-phase system), the yield of αω-dichloro-oligosiloxane falls and the amount of unreacted dichlorodimethylsilane increases. At the same time octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) appear in the reaction mixture.

The increase of the content of higher oligomers in the reaction mixture is promoted by a decrease of the $(CH_3)_2SiCl_2 : H_2O$ molar ratio from 2 to 1.8–1.5.[11] For the ratio 1.5:1, the yield of oligomers with $n \geqslant 3$ increases by a factor greater than 2.

Hydrolysis of dichlorodimethylsilane or dichloromethylsilane in ether at −70°C yielded αω-dichloro-oligodimethylsiloxanes with $n = 1-3$ [12] or $1-5$ [13] and αω-dichloro-oligomethylsiloxanes $Cl(CH_3SiHO)_nSi(CH_3)HCl$ with $n = 1-4$ [13] respectively.

When a 1 : 18 : 1 (wt.%) mixture of $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and CH_3SiCl_3 was treated with a 62% solution of hydrogen chloride in water under pressure, 1,3-dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane were obtained in yields of 33.4 and 20.4% respectively[14].

$\alpha\omega$-Dichloro-oligomethylphenylsiloxanes have been obtained by the hydrolysis of dichloromethylphenylsilane with a deficiency of water in the presence of a solvent[15]. Under optimum conditions, the yields of oligomers containing 2, 3, 4, 5, and 6 silicon atoms in the molecule were 32, 25, 7, 4, and 4% respectively; 21% of $CH_3(C_6H_5)SiCl_2$ does not react. The reaction mixture also contains *sym*-trimethyltriphenyl cyclotrisiloxane and *sym*-tetramethyltetraphenylcyclotetrasiloxane.

Hydrolysis without a solvent results in the formation of only 8% of a mixture of distillable oligomers containing 2% of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane and 47% of higher $\alpha\omega$-dichloro-oligosiloxanes. The amount of unreacted $CH_3(C_6H_5)SiCl_2$ increases to 45%.

1,3-Dichloro-1-methyl-1,3,3-triphenyldisiloxane was obtained by the simultaneous hydrolysis of dichloromethylphenylsilane and dichlorodiphenylsilane in toluene at 80°C.[16] 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisiloxane is formed when moist dichloromethylphenylsilane is distilled (yield 16.4%)[17] or in the hydrolysis of $Cl(CH_3)C_6H_5Si(OC_6H_4C_6H_5\text{-}o)$[18]. $\alpha\omega$-Dichloro-oligodiphenylsiloxanes have been obtained by the hydrolysis of dichlorodiphenylsilane[19,20]. With a $(C_6H_5)_2SiCl_2 : H_2O$ molar ratio of 2 : 1, mainly 1,3-dichlorotetraphenyldisiloxane and 1,5-dichlorohexaphenyltrisiloxane are formed[19]. At the same time the formation of hexaphenylcyclotrisiloxane is observed. When the reactant ratio is reduced to 1.5, the yield of 1,3-dichlorotetraphenyldisiloxane falls and the yields of 1,5-dichlorohexaphenyltrisiloxane and hexaphenylcyclotrisiloxane increase. The theoretical yield of cyclosiloxane is reached when the $(C_6H_5)_2SiCl_2 : H_2O$ molar ratio is reduced to 1 – 0.67.

Hydrolysis of dichloromethylsilanes with an organic substituent, of the type $CH_3(RCH_2CH_2)SiCl_2$ (R = CF_3 or C_3F_7), in an autoclave by water saturated with hydrogen chloride (24 – 30°C, 28 – 48 h) yielded $\alpha\omega$-dichlorooligomethylsiloxanes with an organic substituent per unit, $Cl[CH_3(RCH_2CH_2)SiO]_nSiCH_3(RCH_2CH_2)Cl$, containing fluorine atoms in the organic group[21]. The oligomer $ClCH_3(CH_2Cl)SiO[CH_3(ClCH_2)SiO]_3SiCH_3(CH_2Cl)Cl$ was obtained similarly[22].

Hydrolysis of dichlorosilanes with two organic substituents can be carried out in the presence of salts of heterocyclic bases, acid amides, or triphenylphosphine. For example, when water is added to a mixture of dichlorodiphenylsilane and $C_5H_5N.HCl$ in toluene [molar ratio $(C_6H_5)_2SiCl_2 : H_2O = 2.5 : 1$] at 80 – 85°C, 1,3-dichlorotetraphenyldisiloxane is formed in 81.5 yield. The residue contains 1,5-dichlorohexaphenyltrisiloxane. $\alpha\omega$-Dichloro-oligomethyl- and $\alpha\omega$-dichloro-oligomethylphenyl-siloxanes were obtained similarly[23].

A conductimetric study of the hydrolysis of chlorosilane in a homogeneous medium (in a mixture of ethylene glycol with ether) showed that a decrease of reaction temperature and an increase of HCl content suppress the hydrolysis of Si – Cl bonds and promote the formation of the corresponding oligomers $Cl(R_2SiO)_nSiR_2Cl$.[24]

Linear $\alpha\omega$-difluoro-oligodiethylsiloxanes $F[(C_2H_5)_2SiO]_nSi(C_2H_5)_2F$ and also 8 – 10% of $(C_2H_5)_2SiF_2$ are formed in the hydrolysis of dichlorodiethylsilane with a saturated aqueous solution of potassium fluoride[25]. The study of the mechanism of the partial hydrolysis of dichlorosilanes with two organic substituents is of great importance for the determination of the optimum conditions in the preparation of $\alpha\omega$-dichloro-oligosiloxanes. This reaction is a complex process and the nature and proportions of the hydrolysis products depend on many factors ($R_2SiCl_2 : H_2O$ ratio, structure of R_2SiCl_2, solvent, reaction temperature, etc.). The formation of linear oligomers is promoted by an increase of the concentration of R_2SiCl_2, the homogeneity of the medium, and a low process temperature. It has been suggested[6,26] that partial hydrolysis is accompanied by a stepwise condensation:

$$Cl(R_2SiO)_nSiR_2Cl + H_2O \rightarrow Cl(R_2SiO)_nSiR_2OH,$$

$$2\,Cl(R_2SiO)_nSiR_2OH \rightarrow Cl(R_2SiO)_{2n+1}SiR_2Cl + H_2O \text{ etc.}$$

Evidence for this mechanism comes from the formation, during the hydrolysis of oligosiloxanes and polysiloxanes with two organic substituents per unit and mainly with a linear structure and from the high polydispersity of the oligomers and polymers obtained.

Low-molecular-weight $\alpha\omega$-dichlorosiloxanes are formed when t-butyl alcohol reacts with dichloromethylphenylsilane[15]. t-Butyl chloride, hydrogen chloride, polyisobutylene, and benzene are formed at the same time. The process is probably based on the hydrolysis of chlorosilanes by the water formed in the reaction of the liberated hydrogen chloride with t-butyl alcohol.

2. Telomerisation of Cyclosiloxanes with Halogenosilanes Having Organic Substituents

The telomerisation of cyclosiloxanes with halogenosilanes having organic substituents, which takes place according to the general mechanism

$$RR'SiCl_2 + n(R''R'''SiO)_x \rightarrow ClRR'Si(OSiR''R''')_{nx}Cl, \quad (x \geqslant 3)$$

was first achieved in 1960.[27-30] The reaction is carried out in sealed tubes (without a catalyst) at 250°C for 3 – 5 h. The difunctional oligomers $ClR(CH_3)Si(OSiR'R'')_{3n}Cl$ (R = R' = R'' = CH_3; R = H, R' = R'' = CH_3; R = CH_2=CH, R' = R'' = CH_3; R = C_6H_5, R' = R'' = CH_3; R = R' = CH_3, R'' = C_6H_5; R = CH_3, R' = R'' = C_6H_5) were obtained in this way from $R(CH_3)SiCl_2$ and $(R'R''SiO)_3$[27,28,30-36]. The reactivities of halogenosilanes and cyclosiloxanes decrease in the series $CH_3SiHCl_2 > (CH_3)_2SiCl_2 > CH_3(CH_2=CH)SiCl_2 > CH_3(C_6H_5)SiCl_2$; $[(CH_3)_2SiO_3] > [(C_2H_5)_2SiO]_3 > [CH_3(C_6H_5)SiO]_3 > [CH_3(CH_2=CH)SiO]_3$. In all cases, instead of individual telomers, their mixtures are formed. A decrease of the molar ratio $RR'SiCl_2 : (R''R'''SiO)_3$ leads to a fall of the yield of low-molecular-weight telomers and a sharp increase of high-boiling telomerisation products.

With an equimolar ratio of dichlorodimethylsilane and hexamethylcyclotrisiloxane (D_3), telomers with $n = 1$ (64.4%), $n = 2$ (15.6%), $n = 3$ (4.1%), and $n \geqslant 4$ (10.9%) were obtained[31]. Telomers with $n = 1$ (83.1%), $n = 2$ (7.1%), $n = 3$ (3.1%), and $n \geqslant 4$ (3.9%) were obtained from dichloromethylsilane and D_3 (in proportions of 1 : 1); with a molar ratio of 1 : 2, the products were telomers with $n = 1$ (31.8%), $n = 2$ (42.8%), $n = 3$ (9.5%) and $n \geqslant 4$ (14.3%).[34] The reaction of dichloromethylvinylsilane with D_3 leads to the formation of a mixture of telomers with $n = 1$ (71.2%), $n = 2$ (11.8%), and $n \geqslant 3$ (8.7%). When the ratio is 1 : 2, the yields of telomers are 67.1% for $n = 2$ and 25.5% for $n \geqslant 3$. The telomer with $n = 1$ is not formed under these conditions[34].

Dichloromethylphenylsilane forms with D_3 (molar ratio 1 : 1) telomers with $n = 1$ (76.2%), $n = 2$ (77.6%), and $n \geq 3$ (13.6%).[34]

When 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane was cleaved by dichlorodimethylsilane, telomers with $n = 1$ (32.9%), $n = 2$ (4.9%), and $n \geq 3$ (63.9%), were obtained. The conversion of siloxane was 88.0% and that of dichlorodimethylsilane 36%.[35] The reaction in an autoclave is accompanied by the dissociation of siloxane bonds in the telomers.

Telomers could not be isolated from the products of the reaction of dichlorodimethylsilane with 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane because of the occurrence of a side process involving polymerisation with participation of the vinyl groups[35].

Hexaethylcyclotrisiloxane is cleaved by dichloromethylsilane with formation of oligomers in which $n = 1$ (64.3%), $n = 2$ (17.6%), and $n \geq 3$ (18.6%).[35] The reaction with dichlorodiethylsilane gives a 61.9% yield of 1,7-dichloro-octaethyltetrasiloxane[37].

1,7-Dichloro-1,3,5,7,7-pentaethyl-1,3,5-tri-n-propyltetrasiloxane (57%) and 1,7-dichloro-1,3,5,7-tetraethyl-1,3,5,7-tetra-n-propyltetrasiloxane (33%) were obtained by the cleavage of *sym*-triethyltri-n-propylcyclotrisiloxane with dichlorodiethylsilane and dichloroethyl-n-propylsilane respectively. 1,3,5,7-Tetra-n-butyl-1,7-dichloro-1,3,5,7-tetraethyltetrasiloxane was synthesised in 42% yield from *sym*-tetra-n-butyltetraethylcyclotrisiloxane and n-butyldichloroethylsilane[38].

D_4 enters into the telomerisation reaction with greater difficulty than D_3. Nevertheless oligomers of the type $ClR(CH_3)Si(OSiR'R'')_nCl$ ($R = R' = R'' = CH_3$; $R = C_6H_5$, $R' = R'' = CH_3$; $R = CH{=}CH_2$, $R' = R'' = CH_3$) have been obtained by the reaction of D_4 with $R(CH_3)SiCl_2$ ($R = CH_3$, C_6H_5, or $CH = CH_2$).[27,39].

When the ratio $D_4 : (CH_3)_2SiCl_2 = 2 : 1$, telomers with $n = 1$ (16.7%), $n = 2$ (20.0%), and $n = 3$ (7.7%) are formed and when the ratio is 1 : 1 the products have $n = 1$ (36.9%), $n = 2$ (33.0%), and $n = 3$ (7.5%). The reaction with a 3 : 1 reactant ratio was also investigated[33]. In all cases a mixture was obtained in which the telomer corresponding to the specified $D_4 : (CH_3)_2SiCl_2$ ratio predominated.

The reaction of equimolar amounts of dichloromethylvinylsilane and D_4 gave telomers with $n = 1$ (18.5%), $n = 2$ (30.8%), $n = 3$ (14.6%), and $n \geq 4$ (36.1%).[39] The reaction of dichloromethylphenylsilane with D_4 under standard conditions (250°C, 3 h) proceeds with the formation of small amounts of telomers (about 10 wt.%). Under more severe conditions (300°C, 5 h, molar ratio 2 : 1), the overall conversion reaches 18% and telomers with $n = 1$ (7.8%) and $n = 2$ (2.3%) are formed[39].

The synthesis of 1,9- dichlorodecamethylpentasiloxane (yield 34%) by heating a 1 : 1 mixture of dichlorotrimethylsilane and D_4 in an enamelled autoclave at 270–400°C and 80 atm has been described[40]. At 300°C the yield increases to 50%.

Changes in reactant ratio and temperature affect the yield of reaction products, which is a maximum for a ratio of 1 : 2 – 81% at 300°C and 77% at 350°C. At 400°C the yield falls to 42%. In all cases side products of the cleavage of the $-Cl[(CH_3)_2SiO]_nSi(CH_3)_2Cl$ chains with $n = 1$–6, 8, or 12 were obtained. When the reaction was carried out in an autoclave without a glass liner, a low yield of the required telomer was obtained together with a large amount of side products.

1,3-Dichlorotetramethyldisiloxane (22%), 1,5-dichlorohexamethyltrisiloxane (19%), 1,7-dichloro-octamethyltetrasiloxane (15%), higher oligomers (26%), and also D_3 (0.2%) and D_4 (1.0%) were obtained by heating polydimethylsiloxane with dichlorodimethylsilane in a bomb (380–400°C 5 h). In the presence of a catalyst ($FeCl_3$ and HCl or HBr), the reaction takes place also at room temperature[41].

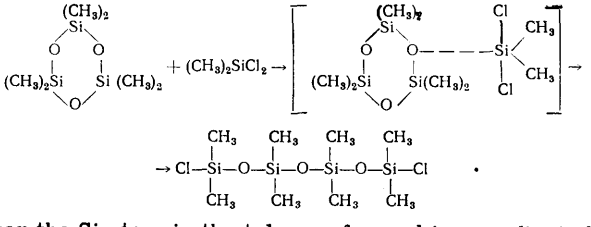
Oligomers containing together with Si–Cl bonds functional groups in the organic substituents were obtained by the reaction of D_3 with alkyl(chloroalkyl)chlorosilanes containing chlorine atoms in the α-, β-, and γ-positions[42] and by the reaction of D_4 with dichloro-(3,3,3-trifluoropropyl)methylsilane[42].

The position of the halogen atom in the hydrocarbon group of dichloro(halogenoalkyl)methylsilanes has a significant influence on the telomerisation reaction[42]. Thus dichloro(chloromethyl)methylsilane reacts with D_3 to form not only the telomers $Cl[(CH_3)_2SiO]_{3n}.SiCH_3(CH_2Cl)Cl$ with $n = 1$ (43.7%) and $n = 2$ and 3 but also their dissociation products containing 2, 3, and 4 silicon atoms in the molecule in yields of 18.3, 16.5, and 12.5% respectively. Dichloro-(2-chloroethyl)methylsilane reacts with D_3 to form telomers in which $n = 1$ (39.1%) and $n = 2$ (10.5%) and dissociation side products. The reaction of dichloro-(3-chloropropyl)methylsilane with D_3 is strictly of the telomerisation type with formation of telomers in which $n = 1$ (63.0%) and $n = 2$ (4.8%). The reactivity of dichloro(chloroalkyl)methylsilanes in the reaction with D_3 falls in the sequence $\beta > \alpha > \gamma$ as the position of the chlorine atom in the alkyl group is varied.

The reaction of D_4 with dichloro-(3,3,3-trifluoropropyl)methylsilane at 250°C involves the formation of a mixture of $Cl[(CH_3)_2SiO]_{4n}SiCH_3.(CF_3CH_2CH_2)Cl$ telomers with $n = 1$ (28.4%), $n = 2$ (7%), and $n = 3$ (10%) for the equimolar reactant ratio and with $n = 1$ (16.2%), $n = 2$ (22%), and $n = 3$ (20%) for the 2 : 1 ratio. The reaction proceeds mainly as in the case of dialkyldichlorosilanes. The polar and steric effects of the 3,3,3-trifluoropropyl group influence only the yield of the telomers. It proved possible to obtain 1,7-dichloro-octamethyltetrasiloxane and 1,9-dichlorodecamethylpentasiloxane by the cleavage of D_4 with dichlorodimethylsilane (molar ratio 1 : 4 – 4 : 1) in the presence of an equimolar amount of dimethylformamide, its derivatives, or *N*-formylpiperidine at 20°C in 120 h.[44]

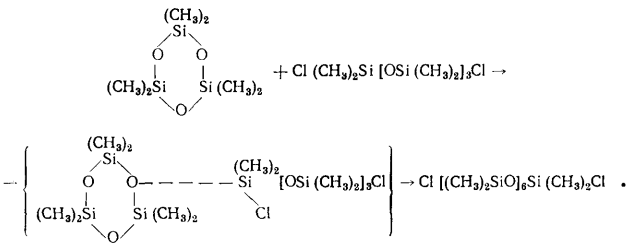
In the presence of a catalyst ($FeCl_3$) the telomerisation reaction is complicated by a side reaction involving the cleavage of telomer ins[36]. The reaction of D_3 with $(CH_3)_2SiCl_2$ results in the formation of the oligomers $Cl[(CH_3)_2SiO]_mSi(CH_3)_2Cl$ in which the number of silicon atoms *m* ranges from 2 to 7. In the presence of $FeCl_3$ linear siloxanes can also enter into the telomerisation reaction with dialkyldihalogenosilanes[45].

The study of the mechanism of the telomerisation reaction[27,32] led to the hypothesis that an intermediate complex of the cyclosiloxane and halogenosilane is formed in the first reaction stage and is subsequently converted into the first member of the homologous series:

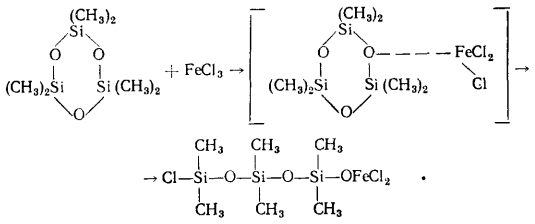


Later the Si atom in the telomer formed is coordinated to the oxygen atom of a new cyclosiloxane molecule as a

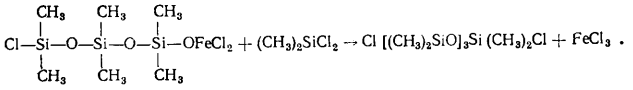
result of which the next member of the homologous series is formed, etc.



In the presence of a catalyst ($FeCl_3$) the reaction becomes reversible[32]. Together with telomers, dissociation products containing 1, 2, 3, and more silicon atoms in the molecule are formed. In this case a molecule of iron(III) chloride is coordinated to the oxygen atom of the cyclosiloxane of the telomer and the resulting complex decomposes via the mechanism



The Si–OFe bond is unstable and under the influence of compounds containing the Si–Cl bond breaks down with liberation of $FeCl_3$ and the formation of the Si–O–Si bond:



3. Cleavage of Cyclosiloxanes by Organic and Inorganic Halogen-containing Compounds

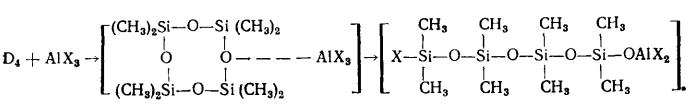
$\alpha\omega$-Dihalogeno-oligodialkylsiloxanes are formed when cyclosiloxanes or linear siloxanes are heated with boron, aluminium, phosphorus, or antimony halides:

$$(RR'SiO)_n + MX_n \rightarrow X(RR'SiO)_mSiRR'X \quad (M=B, Al, P, Sb) .$$

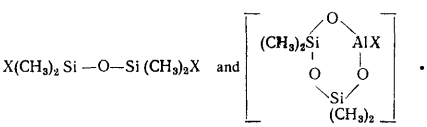
For example, oligomers of the $Cl(RR'SiO)_nSiRR'Cl$ series, where $R = R' = CH_3$,[46] $R = R' = C_2H_5$,[46,47] or $R = CH_3$ and $R' = C_6H_5$,[47] were obtained by the cleavage of the corresponding cyclotrisiloxanes and cyclotetrasiloxanes with aluminium chloride.

Difficult to obtain $\alpha\omega$-dibromo-oligosiloxanes, for example 1,3-dibromotetramethyldisiloxane, 1,5-dibromohexamethyltrisiloxane, and 1,7-dibromo-octamethyltetrasiloxane, have been synthesised by the reaction of D_4 with $AlBr_3$.[48] 1,3-Difluoro- and 1,3-dichlorotetramethyldisiloxanes are formed when cyclosiloxanes are cleaved with BF_3 or BCl_3 respectively[49,50].

It is suggested[48] that the first stage of the reaction of cyclosiloxanes with $AlCl_3$ and $AlBr_3$ is, as in the telomerisation in the presence of $FeCl_3$, the coordination of the oxygen atom of the cyclosiloxane to $AlCl_3$ or $AlBr_3$ with subsequent ring opening:

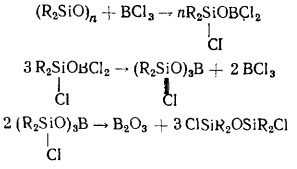


The linear aluminosiloxane formed decomposes into



Under the influence of AlX_3, 1,3-dihalogenotetramethyldisiloxane rearranges to higher $\alpha\omega$-dihalogenopolysiloxanes[48].

It has been suggested[50] that the dialkylchlorosiloxyborates formed initially in the reaction with BCl_3 decompose into the corresponding chlorosiloxanes and B_2O_3:



$\alpha\omega$-Dichloro-oligosiloxanes are also obtained by the distillation of cyclic or linear polysiloxanes with phosphorus oxide halides, antimony halides, or the halides of aromatic acids (benzoyl, phthaloyl, or isophthaloyl chlorides) in the presence of $FeCl_3$.[51]

$\alpha\omega$-Dichloro-oligoalkylmethylsiloxanes, in which the alkyl group contains three and more fluorine atoms, have been obtained by the cleavage with hydrochloric acid (at 30°C and an elevated pressure) of the hydrolysis product of $CH_3(RCH_2CH_2)SiCl_2$ ($R = CF_3$ or C_3F_7).[21]

4. Heterofunctional Condensation Reactions

The heterofunctional condensation reaction, which proceeds according to the general mechanism $\equiv Si-X + RO-Si\equiv \rightarrow \equiv Si-O-Si\equiv$ where X = halogen and R = H, alkyl, or acyl, has been less frequently used to synthesise $\alpha\omega$-difunctional oligomers than the hydrolysis of chlorosilanes with organic substituents and the cleavage of cyclosiloxanes. An advantage of this method over those described above is the possibility of obtaining oligomers with a specified alternation of different substituents at the Si atoms.

When dichloromethylsilane, dichlorodimethylsilane, dichloroethylsilane and dichlorodiethylsilane are heated with chloroethoxydimethylsilane (60–80°C, $FeCl_3$ catalyst), the corresponding $\alpha\omega$-dichloro-oligodialkylsiloxanes containing both identical and mixed alkyl substituents are formed[52]:

$$R_2SiCl_2 + R_2SiCl(OR) \rightarrow Cl(SiR_2O)SiR_2Cl + n\,HCl .$$

The reaction proceeds according to the mechanism

$$ClSiR_2-Cl + C_2H_5O-SiR_2'-Cl \rightarrow ClSiR_2-O-SiR_2'Cl + C_2H_5Cl ,$$

$$ClSiR_2OSiR_2'Cl + C_2H_5O-SiR_2'-Cl \rightarrow ClSiR_2-OSiR_2'-O-SiR_2'Cl + C_2H_5Cl , \text{ etc.}$$

The oligomers $Cl[(CH_3)_2SiO]_nSi(CH_3)_2Cl$ with $n = 1-3$ have been obtained by this method from dichlorodimethylsilane and chloroethoxydimethylsilane (1 : 1 molar ratio) in proportions analogous to those obtained in the partial hydrolysis of dichlorodimethylsilane [$n = 1$ (28%), $n = 2$ (24%), $n = 3$ (15%), and $n = 5$ and 6 (2%)][9,10]; 22% of the initial $(CH_3)_2SiCl_2$ does not react, whereas $(CH_3)_2Si(OC_2H_5)Cl$ reacts completely. The formation of cyclosiloxanes was not observed.

The reaction of dichlorodiethylsilane with chloroethoxydimethylsilane (1 : 1) leads to the corresponding $\alpha\omega$-dichloro-oligodialkylsiloxanes containing preferentially 4 and 5 silicon atoms in the molecule.

When the concentration of $(C_2H_5)_2SiCl_2$ is increased (up to a molar ratio of 2 : 1), the yield of low-molecular-weight $\alpha\omega$-dichloro-oligosiloxanes $Cl[(CH_3)_2SiO]_nSi(C_2H_5)_2Cl$, containing between 2 and 5 silicon atoms [$n = 1$ (14%), $n = 2$ (13.7%), and $n = 3$ (5%)], increases. In the case of dichloromethylsilane and dichloroethylsilane, the main heterofunctional condensation reaction is accompanied by disproportionation[52]:

$$CH_3SiHCl_2 + (CH_3)_2Si(OC_2H_5)Cl \rightarrow CH_3SiH(OC_2H_5)Cl + (CH_3)_2SiCl_2 .$$

The extremely reactive chloroethoxymethylsilane readily reacts with alkyldichlorosilanes[52]:

$$CH_3HSi(OC_2H_5)Cl + CH_3SiHCl_2 \rightarrow Cl(CH_3)SiHOHSi(CH_3)Cl + C_2H_5Cl .$$

Apart from the main products of the heterofunctional condensation of dichloromethylsilane and dichloroethylsilane with chloroethoxydimethylsilane

$Cl[(CH_3)HSiO]_nSi(CH_3)_2Cl$ [$n = 1$ (10%) and $n = 2$ (2.2%)] and $Cl[(C_2H_5)HSiO]_nSi(CH_3)_2Cl$ [$n = 1$ (7.7%) and $n = 2$ (8.8%)], the products $Cl[(CH_3)HSiO]_nSi(CH_3)HCl$ [$n = 1$ (18.3%) and $n = 2$ (6.2%)] and $Cl[(C_2H_5)HSiO]_nSi(C_2H_5)HCl$ [$n = 1$ (8.1%) and $n = 2$ (3.3%)] were also isolated.

Heterofunctional condensation of silanediols containing two organic substituents with dichlorosilanes (1 : 2), also containing two organic substituents, in the presence of aniline yielded the corresponding hexa-alkyl-1,5-dichlorotrisiloxanes[53]:

$$2\,RR'SiCl_2 + R''R'''Si(OH)_2 \rightarrow ClSiRR'OSiR''R'''OSiRR'Cl + 2\,HCl$$

($R = R' = CH_3$, $R'' = C_6H_5$, $R''' = CH_3$; $R = R' = C_6H_5$, $R'' = R''' = CH_3$; $R = R' = C_6H_5$, $R'' = C_6H_5$, $R''' = CH{=}CH_2$; $R = R' = C_6H_5$, $R'' = CH_3$, $R''' = C_2H_5$; $R = R' = C_6H_5$, $R'' = CH_3$, $R''' = CH_2CH(CH_3)C_6H_5$; $R = R' = C_6H_5$, $R'' = CH_3$, $R''' = CH_2CH_2CF_3$).

1,5-Dichloro-1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane is formed in 66% yield on condensation of diphenylsilanediol with dichlorodimethylsilane (1 : 2) in the presence of a solvent and a hydrogen chloride acceptor (pyridine)[54].

5. Other Reactions

Dialkyldihalogenosilanes can react with metal oxides whereby they are converted into $\alpha\omega$-dihalogenosiloxanes. Metal oxides serve as a source of oxygen necessary for the formation of the Si–O–Si bond. Dichlorodimethylsilane reacts with Fe_2O_3 to form 1,3-dichlorotetramethyldisiloxane[55]. However, according to other data[56], anhydrous Fe_2O_3 does not react with $(CH_3)_2SiCl_2$ to form the above compound and therefore its synthesis requires the addition of a small amount of water. Instead of water, one can introduce at the beginning of the reaction a small amount of hydrogen chloride. Evidently chlorodimethylsilanol is formed in the first stage as a result of the hydrolysis of $(CH_3)_2SiCl_2$. Subsequently Fe_2O_3 apparently behaves as an acceptor of hydrogen chloride and a donor of water promoting the heterofunctional condensational reaction:

$$R_2SiCl_2 + H_2O \rightarrow R_2Si(Cl)OH + HCl ,$$
$$3\,R_2Si(Cl)OH + 3\,R_2SiCl_2 + 0.5\,Fe_2O_3 \rightarrow 3\,ClR_2SiOSiR_2Cl + FeCl_3 + 1.5\,H_2O .$$

The reaction of chlorodimethylsilanol with $(CH_3)_2SiCl_2$, which leads to the formation of oligomers, takes place according to the mechanism

$$Cl(CH_3)_2SiOH + (CH_3)_2SiCl_2 \xrightarrow{Fe_2O_3} Cl(CH_3)_2SiOSi(CH_3)_2Cl + HCl ,$$
$$Cl(CH_3)_2SiOH + Cl(CH_3)_2SiOSi(CH_3)_2Cl \rightarrow Cl(CH_3)_2SiOSi(CH_3)_2OSi(CH_3)_2Cl + HCl \text{ etc.}$$

PbO, CaO, MgO, ZnO, CuO,[57,58] BeO, and Ag_2O[58] have also been used as oxygen donors.

Dichlorodimethylsilane reacts with ethanol in the presence of catalytic amounts of $FeCl_3$, forming 1,2-dichlorotetramethyldisiloxane [up to 69% of $(CH_3)_2SiCl_2$ which has reacted] and 1,5-dichlorohexamethyltrisiloxane (21%).[59]

The mechanism of the catalytic effect of iron(III) chloride probably consists of the following steps:

$$3\,C_2H_5OH + FeCl_3 \rightarrow 3\,C_2H_5Cl + Fe(OH)_3 ,$$
$$3\,Fe(OH)_3 + 3\,HCl \rightarrow FeCl_3 + 3H_2O .$$

An interesting method for the preparation of chlorooligomers is based on the chlorination of hydrosiloxanes containing linkages between H and Si atoms[60,61], for example:

$$H[(CH_3)_3SiO]_2SiO\{SiO[OSi(CH_3)_3]_2\}_nSi[OSi[OSi(CH_3)_3]_2H \quad (n \geqslant 0)$$

or

$$HR(CH_3)Si\{OSi[OSi(CH_3)_3]_2\}_nOSi(CH_3)RH \quad (R = CH_3, C_6H_5 \text{ и } n \geqslant 1) .$$

III. METHODS OF SYNTHESIS OF $\alpha\omega$-DIACYLOXYOLIGOSILOXANES

1. The Cleavage of Cyclosiloxanes by Carboxylic Acid Anhydrides and Diacetoxydimethylsilane

$\alpha\omega$-Diacyloxyoligosiloxanes have been little investigated compared with other organosilicon oligomers. At the same time $\alpha\omega$-diacyloxysiloxanes containing reactive acyloxy-groups at the end of the chain are very promising and interesting oligomers from which it is possible to obtain a large number of a wide variety of organosilicon compounds.

The most important method of synthesising $\alpha\omega$-diacyloxyoligosiloxanes containing two organic substituents per unit consists in the cleavage of cyclosiloxanes by carboxylic acid anhydrides.

Acetic anhydride cleaves cyclosiloxanes containing two organic substituents (preferably in the presence of catalysts), forming $\alpha\omega$-diacetoxyoligosiloxanes with two organic substituents per unit:

$$(R_2SiO)_n + (CH_3CO)_2O \rightarrow CH_3COO(R_2SiO)_nCOCH_3 .$$

For example, $\alpha\omega$-diacetoxyoligodimethylsiloxanes $CH_3COO[(CH_3)_2SiO]_n.COCH_3$ ($n = 2$ or 3) are formed on catalytic cleavage of D_4 by acetic anhydride (molar ratio about 1 : 5) in the presence of sulfuric acid[62]. A deficiency of this method is the low conversion of D_4 (about 60%), the long duration of the reaction (40 h), and the high yield of diacetoxydimethylsilane, which constitutes about one third of all the reaction products. This reaction is of little interest for the synthesis of diacetoxydimethylsilane, since the latter can be readily obtained directly from dichlorodimethylsilane and acetic anhydride (see, for example, Dolgov et al.[63]).

The use of anhydrous iron(III) chloride or zinc chloride[64–66] as catalysts permits an increase of the conversion of D_4 to 95% and a reduction of the reaction time

to 1.5–4 h. Then oligomers with four and five silicon atoms in the molecule appear in the mixture and the overall yield of oligomers increases [$n = 2$ (20%), $n = 3$ (14%), $n = 4$ (11%), and $n = 5$ (6%); the yields are given relative to the initial reactants]. Diacetoxydimethylsilane is formed in yields up to 5%.

The reaction of D_4 with acetic anhydride involving the formation of $\alpha\omega$-diacetoxyoligodimethylsiloxanes can take place also in the absence of catalysts, provided that it is carried out at 250–260°C under pressure (in an autoclave or a sealed glass tube)[67]. The composition of the oligomers obtained in the autoclave is approximately the same as in the cleavage of D_4 by acetic anhydride in the presence of $FeCl_3$. In the reaction in a sealed glass tube the amount of oligomer with $n = 2$ is lower and that of the oligomer with $n = 5$ somewhat higher [$n = 2$ (14.3%), $n = 3$ (10%), $n = 4$ (9.8%), and $n = 5$ (9.6%)].

$\alpha\omega$-Diacetoxyoligosiloxanes with two organic substituents per unit, containing 3,3,3-trifluoropropyl, ethyl, vinyl, and phenyl groups at the silicon atoms, were obtained similarly from the corresponding cyclosiloxanes $(RR'SiO)_m$ and acetic anhydride[68,69]. The yields of the oligomers are given in Table 1. The conversion of octaethylcyclotetrasiloxane and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane is 85–90%. 1,3,5-Trimethyl-1,3,5-triphenylcyclotrisiloxane cannot be isolated from the reaction mixture, since the reaction products begin to decompose on distillation under the influence of the high temperature and the $FeCl_3$ present even before the distillation of the cyclosiloxane begins.

Table 1. Composition of mixtures of $\alpha\omega$-diacetoxysiloxanes with two organic substituents $[CH_3COO(RR'SiO)_nCOCH_3]$ formed when $(RR'SiO)_m$ is cleaved with acetic anhydride[69].

$CH_3COO(RR'SiO)_nCOCH_3$	R=CH₃; R'=CF₃CH₂CH₂		R=CH₃ R'=CH₂=CH	R=R'=C₆H₅	R=CH₃ R'=C₆H₅
	m=3	m=4*	m=4	m=3+4	m=3
n=2	17.7	8.3	11.4	30.3	14.8
n=3	23.0	36.1	12.1	19.7	8.1
n=4	15.2	9.7	10.9	10.9	—
n=5	—	—	2.8	—	—

* The reaction was carried out in an autoclave in the absence of $FeCl_3$.

1,3,5-Tri-(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane is completely cleaved by acetic anhydride, while 1,3,5,7-tetra-(3,3,3-trifluoropropyl)-1,3,5,7-tetramethylcyclotetrasiloxane is cleaved only to the extent of 30%. When the reaction is carried out in an autoclave (without a catalyst) at 250–260°C, the tetrasiloxane is cleaved almost completely.

When $HClO_4$ is employed as a catalyst, the temperature of the reaction in which cyclosiloxanes are cleaved by acetic anhydride may be reduced[70]. For example, when acetic anhydride is allowed to react with hexaethylcyclotrisiloxane (molar ratio 1 : 1) in the presence of perchloric acid, 1,3-diacetoxyhexaethyltrisiloxane is formed in a yield up to 30% even at room temperature. 1,3-Diacyloxytrisiloxanes with six organic substituents, $R'COO[C_2H_5(R)SiO]_3COR'$, were obtained by the cleavage of the corresponding cyclosiloxanes by carboxylic acid anhydrides in the presence of $ZnCl_2$ at 100°C or without a catalyst at 250°C (in a sealed tube)[70]. The yields of the oligomers are given in Table 2.

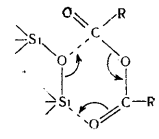
Boron triacetate has also been used as a catalyst of the cleavage of polysiloxanes by carboxylic acid anhydrides[71].

Oligodimethylsiloxanes blocked by perfluoroacyloxy-groups have been obtained by the cleavage of D_4 with perfluorocarboxylic acid anhydrides (in a sealed glass tube)[72]. With a D_4 : heptafluorobutyric acid anhydride molar ratio of 1 : 1, the cleavage products are the oligomers $CF_3CF_2CF_2COO[(CH_3)_2SiO]_nCOCF_2CF_2CF_3$ with $n = 2$ (27%) and $n = 4$ (30%) and also a mixture of oligomers with $n = 5$ and 6. When the ratio of the initial reactants is increased to 9 : 1, a viscous liquid polymer with $\bar{M} = 3840$ is formed. A similar polymer was obtained also in the reaction of D_4 with trifluoroacetic acid anhydride (molar ratio 10 : 1). When D_4 was cleaved with butyric anhydride, a mixture of oligomers with $n = 2$ (25.8%), $n = 3$ (14.8%), and $n \simeq 7$ (57%) was obtained.

Table 2. The yield of $R'COO[C_2H_5(R)SiO]_3COR'$ obtained by the cleavage of $[C_2H_5(R)_3SiO]_3$ with $(R'CO)_2O$.[70]

R	R'	Yield of trisiloxane, %		R	R'	Yield of trisiloxane, %	
		in sealed tube 250°C	in the presence of $ZnCl_2$ at 100°C			in sealed tube 250°C	in the presence of $ZnCl_2$ at 100°C
C_2H_5	CH_3	33.0	63.5	C_2H_5	C_2H_5	22.4	44.8
CH_3	CH_3	—	28.1	C_2H_5	C_4H_9	29.2	41.0
C_3H_7	CH_3	16.8	42.0	C_2H_5	C_6H_{11}	20.7	46.8

The cleavage of cyclosiloxanes by carboxylic acid anhydrides is probably reversible. The composition of the products of the reaction of D_4 with acetic anhydride is independent of the nature of the initial cyclosiloxane (D_3, D_4, D_5, "depolymerisation mixture", and a mixture of cyclic and linear siloxanes) and is determined only by the ratio of the initial reactants[66]. It has been suggested[73] that the cleavage of siloxanes proceeds via the intermediate formation of a six-membered cyclic activated complex involving the Si–O bond and the reactant. As a result of the delocalisation of six electrons in the ring formed, the energy required for the activation of the molecule diminishes, which facilitates cleavage. Similarly, in the cleavage of cyclosiloxanes by acid anhydrides, an intermediate cyclic complex is formed in the first reaction stage (with or without the participation of the catalyst):



which on decomposition gives rise to an $\alpha\omega$-diacyloxysiloxane oligomer with the same number of silicon atoms as in the initial ring:

$$(R_2SiO)_n + (R'CO)_2O \rightarrow R'COO(R_2SiO)_nCOR' .$$

The formation of homologues of this oligomer with a greater or smaller number of silicon atoms in the linear chain takes place via the following reactions.

1. Homofunctional condensation via the acyloxy-groups:

$$2\,R'COO(R_2SiO)_nCOR' \rightarrow R'COO(R_2SiO)_{2n}COR' + (R'CO)_2O .$$

2. Cleavage of the cyclosiloxane by a diacyloxysilane or a diacyloxysiloxane:

$$(R_2SiO)_n + R'COO(R_2SiO)_mCOR' \rightarrow R'COO(R_2SiO)_{n+m}OCOR'.$$

3. Cleavage of the $\alpha\omega$-diacyloxysiloxane by a carboxylic acid anhydride:

$$R'COO(R_2SiO)_nCOR' + (R'CO)_2O \rightarrow R'COO(R_2SiO)_mCOR' + R'COO(R_2SiO)_{n-m}COR'.$$

4. Redistribution of the chains (mutual cleavage) of two molecules of $\alpha\omega$-diacyloxysiloxanes:

$$R'COO(R_2SiO)_nCOR' + R'COO(R_2SiO)_mCOR' \rightarrow R'COO(R_2SiO)_kCOR' + RCOO(R_2SiO)_pCOR'.$$

The possibility of such reactions has been confirmed as follows. When diacetoxymethylphenylsilane is heated at 200–260°C, acetic anhydride and cyclic polymethylphenylsiloxanes are formed[74]. Heating of individual $\alpha\omega$-diacetoxydimethylsiloxanes containing between two and five silicon in the molecule and of diacetoxydimethylsilane, both in the presence of a catalyst and without it, leads to the formation of $\alpha\omega$-diacetoxyoligodimethylsiloxanes both with a smaller and a greater number of silicon atoms compared with the initial oligomer[75,76]. The reaction mixture contains acetic anhydride and a small amount of cyclosiloxanes.

$\alpha\omega$-Diacyloxysiloxanes with two organic substituents are formed from cyclosiloxanes (D_3 and D_4) and acyloxysilanes or acyloxysiloxanes in the presence of catalysts (aprotic Lewis acids)[77]. Thus the reaction of D_3 with diacetoxydimethylsilane in the presence of $ZnCl_2$ yielded 1,7-diacetoxyoctamethyltetrasiloxane and 1,13-diacetoxytetradecamethylheptasiloxane. In the absence of a catalyst, high-molecular-weight polysiloxanes are formed.

2. Cleavage of Cyclosiloxanes by Carboxylic Acid Halides

$\alpha\omega$-Diacetoxyoligodimethylsiloxanes are the main products of the cleavage of D_4 by acetyl halides (acetyl chloride and fluoride)[78,79]. The reaction proceeds both in the presence of a catalyst ($FeCl_3$) and without it (in an autoclave). At the same time the corresponding dihalogenodimethylsilane and 1,3-dihalogenotetramethyldisiloxane are formed:

$$(R_2SiO)_4 + CH_3COX \rightarrow CH_3COO(R_2SiO)_nCOCH_3 + X(R_2SiO)_mSiR_2X,$$

where R = CH_3, X = Cl or F, n = 1–5, and m = 0 or 1.

3. Exchange Reactions of the Terminal Groups and Heterofunctional Condensation

These reactions are less important for the preparation of $\alpha\omega$-diacyloxyoligosiloxanes than those described previously, since they require a preliminary synthesis of oligosiloxanes containing other functional groups at the end of the chain. Nevertheless exchange reactions are employed for the synthesis of specific individual oligomers in high yields.

Reactions involving the substitution of Cl atoms by acyloxy-groups in the corresponding $\alpha\omega$-dichloro-oligosiloxanes by treating the latter with carboxylic acid anhydrides[80–82] or carboxylic acid salts[83,84] are most often used. Thus 1,3-diacetoxytetramethyldisiloxane and 1,5-diacetoxyhexamethyltrisiloxane are formed in yields of 60–75%[80] and 82–86%[81] on heating 1,3-dichlorotetramethyldisiloxane or 1,5-dichlorohexamethyltrisiloxane with acetic anhydride (in proportions of 1 : 2), with simultaneous distillation of the acetyl chloride formed:

$$Cl[(CH_3)_2SiO]_nSi(CH_3)_2Cl + 2(CH_3CO)_2O \rightarrow$$
$$\rightarrow CH_3COO[(CH_3)_2SiO]_nSi(CH_3)_2COCH_3 + 2CH_3COCl.$$

1,7-Diacetoxyoctamethyltetrasiloxane and 1,9-diacetoxydecamethylpentasiloxane were obtained similarly in 86% yield[81].

The products of the reaction of the corresponding $\alpha\omega$-dichloromethylphenylsiloxanes with acetic anhydride are $\alpha\omega$-diacetoxyoligomethylphenylsiloxanes[82]. $\alpha\omega$-Diacetoxydimethylsiloxanes containing at the ends of the chain acryloyloxy- or methacryloyloxy-groups are formed in yields up to 90% when an $\alpha\omega$-dichloro-oligosiloxane containing a sulphate group, $Cl[(CH_3)_2SiO]_{7.4}[(CH_3)_2SiOSO_2O]_{0.17}SiR_2Cl$, reacts with potassium methacrylate or acrylic acid[84].

The reaction of oligosiloxane-$\alpha\omega$-diols with carboxylic acids, their anhydrides, and chlorides has been described[83]:

$$HO(R_2SiO)H + 2R'COX \rightarrow R'COO(R_2SiO)_nCOR' + HX\ (X=OH,Cl,OCOR').$$

Heterofunctional condensation of dialkyl(aryl)silanediols with dialkyl(aryl)diacetoxysilanes in the presence of a solvent and an acetic acid acceptor (pyridine) makes it possible to obtain diacetoxytrisiloxanes $RR'Si[OSi(R''R''')OCOCH_3]_2$ [53] (R = R' = C_6H_5, R'' = C_6H_5, R''' = CH_3 or R'' = R''' = CH_3; R = CH_3, R' = $CH{=}CH_2$, R'' = R''' = CH_3; R = C_6H_5, R' = CH_3, R'' = R''' = C_6H_5) in yields up to 90%.

High-molecular-weight $\alpha\omega$-diacetoxypolysiloxanes are formed when poly(siloxane-$\alpha\omega$-diols) are condensed with acetic anhydride or with a diacetoxysilane (diacetoxysiloxane) containing two organic substituents in the presence of nitrogenous bases[85].

4. Homofunctional Condensation

On heating, diacetoxydimethylsilane can condense with the formation of $\alpha\omega$-diacetoxyoligosiloxanes[75,76]. Thus, when $(CH_3)_2Si(OCOCH_3)_2$ was heated with $FeCl_3$ at 150°C, diacetoxyoligosiloxanes with n = 2 (27.7%), n = 3 (11.5%), and n = 4 (5%) were obtained.

Since diacetoxydimethylsilane is readily formed from dichlorodimethylsilane, there is a possibility of synthesising oligomers directly from dichlorodimethylsilane. The latter is heated with acetic anhydride until the evolution of the theoretical amount of acetyl chloride, then $FeCl_3$ is added, and, after heating, $\alpha\omega$-diacetoxyoligodimethylsiloxanes are distilled off[75]:

$$(CH_3)_2SiCl_2 + (CH_3CO)_2O \xrightarrow{-CH_3COCl} (CH_3)_2Si(OCOCH_3)_2 \xrightarrow{FeCl_3} \rightarrow CH_3COO[(CH_3)_2SiO]_nCOCH_3 + (CH_3CO)_2O.$$

The homofunctional condensation of $\alpha\omega$-diacyloxyoligosiloxanes was mentioned in section III, 1.

IV. METHODS OF SYNTHESIS OF $\alpha\omega$-DIALKOXYOLIGOSILOXANES

1. Cleavage of Cyclosiloxanes by Alcohols and Alkoxysilanes

$\alpha\omega$-Dialkoxyoligosiloxanes with two organic substituents can be obtained directly from cyclosiloxanes by their catalytic cleavage with alcohols: $(R_2SiO)_n + 2R'OH \rightarrow R'O(R_2SiO)_nR' + H_2O$; acids[86–88], alkalis[86], or amines[89,90]

may be employed as catalysts for this reaction. For example, hexamethyl-1,5-di-n-octyloxytrisiloxane and hexaethyl-1,5-di-n-octyloxytrisiloxane were obtained by the cleavage of the corresponding cyclotrisiloxanes and cyclotetrasiloxanes (containing organic substituents) by n-octyl alcohol in the presence of an acid (toluene-*p*-sulphonic acid) or an alkaline (sodium methoxide) catalyst with simultaneous distillation of the water formed[86]. The best yield is achieved when the reaction is stopped after distilling off only 33% of the theoretical amount of water formed in the reaction and removing the catalyst.

When 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane is heated with alcohols in the presence of hydrochloric acid or KIL activated clay, 1,5-dialkoxymethylphenylsiloxanes $RO[CH_3(C_6H_5)SiO]_3R$ (R = C_2H_5, n-C_3H_7, or iso-C_3H_7) are formed in yields up to 72–86% [87]. Hydrochloric acid, perchloric acid, or an aluminosilicate may be employed as catalysts[88]. The reaction is significantly influenced by the size of the cyclosiloxane ring, the nature of the substituents at the silicon atoms, and the catalyst. Hexa-alkylcyclotrisiloxanes containing a strained six-membered ring are cleaved more readily than the unstrained octa-alkylcyclotetrasiloxanes.

When $[CH_3(C_6H_5)SiO]_3$ is cleaved with alcohols, individual alkoxy-derivatives are formed, whereas the cleavage of $[CH_3(C_6H_5)SiO]_4$ gives a polydisperse mixture. This is because the rate of cleavage of 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane is comparable to the rates of the secondary processes (reactions of the alcohol with the alkoxysiloxanes)[87]. However, the effect of ring size is somewhat reduced when sodium methoxide is employed as a catalyst[86].

In the presence of an acid catalyst, cyclosiloxanes can be arranged in the following sequence in terms of their decreasing reactivity with respect to alcohols: $D_3 > D_4 >$ hexaethylcyclotrisiloxane > octaethylcyclotetrasiloxane > octaphenylcyclotetrasiloxane. In the presence of an alkoxide, the order of the reactivities of cyclosiloxanes alters somewhat: $D_3 = D_4 >$ hexaethylcyclotrisiloxane > octaphenylcyclotetrasiloxane > octaethylcyclotetrasiloxane, i.e. the rate of cleavage of octaphenylcyclotetrasiloxane becomes higher than that of octaethylcyclotetrasiloxane. The explanation is that in acid cleavage the inductive and steric effects of phenyl groups reduce the reactivity of the siloxane bond in relation to the electrophilic agent by decreasing the electron density at the oxygen atom and screening the Si–O bond (by the phenyl groups).

In alkaline cleavage the inductive effect of phenyl groups promotes a nucleophilic attack on the Si atom, while the inductive and steric effects of ethyl groups hinder it[86].

When an excess of alcohol is used, cyclosiloxanes are completely cleaved to the corresponding dialkoxysilanes with two other organic substituents[90]:

$$1/n\,(R_2SiO)_n + 2R'OH \xrightarrow{R'O^-} R_2Si(OR')_2 + H_2O\ .$$

1,3-Dibutoxytetramethyldisiloxane is formed in a yield of up to 40% when D_4 is heated with tetrabutyl orthotitanate at 200°C for 4 h. Dibutoxydimethylsilane and a polymer are formed at the same time[91].

$\alpha\omega$-Alkoxyoligosiloxanes can be obtained also by the reaction of cyclic or linear polydimethylsiloxanes with alkoxysilanes[92]. For example the reaction of a linear polydimethylsiloxane with tri-n-butoxymethylsilane catalysed by KOH yielded tetra-n-butoxy-1,3-dimethyldisiloxane and penta-n-butoxy-1,3,5-trimethyltrisiloxane:

$$[-Si(CH_3)_2OSi(CH_3)_2]_n + CH_3Si(OC_4H_9\text{-}n)_3 \rightarrow (n\text{-}C_4H_9O)_2Si(CH_3)OSi(CH_3)(OC_4H_9\text{-}n)_2 + (n\text{-}C_4H_9O)_2Si(CH_3)OSi(CH_3)(OC_4H_9\text{-}n)OSi(CH_3)(OC_4H_9\text{-}n)_2\ .$$

2. Reactions of Silanes Containing Two organic substituents and Two Functional Groups at the Silicon Atom and Oligosiloxanes with Two Organic Substituents per Unit.

$\alpha\omega$-Dialkoxyoligosiloxanes can be obtained by the partial hydrolysis of dialkoxydialkylsilanes or $\alpha\omega$-dialkoxyoligosiloxanes, by the esterification of $\alpha\omega$-dichlorooligosiloxanes, by homo- and hetero-functional condensation of the corresponding monomers or oligomers, and also by the hydrosilylation of the corresponding unsaturated compounds.

Dialkoxydialkylsilanes are less reactive than the corresponding dialkyldichlorosilanes and are more difficult to hydrolyse. Nevertheless, on heating in aqueous alcohol in the presence or absence of catalysts, they form the corresponding $\alpha\omega$-dialkoxyoligosiloxanes and a certain amount of cyclosiloxanes and polysiloxanes. Thus, when diethoxydiethylsilane was heated (10 h at 90°C) in alcohol with different amounts of water, the oligomers $C_2H_5O[(C_2H_5)_2SiO]_nC_2H_5$ with $n = 4$ (30.3%), $n = 7$ (76.3%), $n = 8$ (74.8%), and $n = 70$ (73.1%) were isolated[93].

$\alpha\omega$-Diethoxyoligo(chloromethyl)methylsiloxanes with $n = 2$, 3, or 4 were obtained by hydrolysing (chloromethyl)diethoxymethylsilane with a small amount of water (in alcohol) or by the esterification of dichloro(chloromethyl)methylsilane (10 h at 75–80°C) [94]. Partial hydrolysis of dibutoxydipentylsilane yields the oligomers $C_4H_9O[(C_5H_{11})_2SiO]_nC_4H_9$ with $n = 1-5$, [95] and that of di-t-butoxymethylphenylsilane gives t-$C_4H_9O[CH_3(C_6H_5)SiO]_nC_4H_9$-t ($n = 1-5$) [96]. 1,3-Dibutoxytetramethyldisiloxane and 1,5-dibutoxyhexamethyltrisiloxane were isolated in very low yields (4.9 and 2.6%) from an alcoholic solution of dibutoxydimethylsilane kept for two days. Only 9.2% of the initial dibutoxydimethylsilane remained[97].

Hydrolysis of $(CH_3)_2Si(OCH_3)_2$ in the presence of a small amount of alkali as a catalyst in 20% aqueous methanol leads to the oligomers $CH_3O[(CH_3)_2SiO]_nCH_3$ ($n = 2-10$) [98], while $C_2H_5O[(CH_3)_2SiO]_nC_2H_5$ ($n = 2-11$) is formed from $(CH_3)_2Si(OC_2H_5)_2$ [99–101]. Cyclosiloxanes were isolated together with the above compounds.

$\alpha\omega$-Dialkoxyoligosiloxanes can be obtained directly from dialkyldichlorosilanes. The oligomers $C_2H_5O[(CH_3)_2SiO]_nC_2H_5$ with $n = 2$ (42%), $n = 3$ (39.2%), and $n = 4$ are formed on simultaneous partial hydrolysis and esterification of dichlorodimethylsilane with 97% ethanol[102]. The analogous reaction with isopropyl alcohol gives iso-$C_3H_7O[(CH_3)_2SiO]_nC_3H_7$-iso ($n = 1-5$) in an overall yield of 65–85%,[103] and the reaction with moist n-butyl alcohol gives 1,3-dibutoxytetramethyldisiloxane and 1,5-dibutoxyhexamethyltrisiloxane[92]. The products of the esterification of dichlorodiethylsilane by methanol are the oligomers $CH_3O[(C_2H_5)_2SiO]_nCH_3$ with $n = 1-4$.[104] The reaction of dichlorodiphenylsilane with ethanol leads to 1,3-diethoxytetraphenyldisiloxane[105].

1,3-Di-n-butoxy-1,3-dimethyl-1,3-di-α-naphthyldisiloxane (37.7%) and 1,5-di-n-butoxy-1,3,5-trimethyl-1,3,5-tri-α-naphthyltrisiloxane (26.7%) were obtained by the esterification with n-butyl alcohol of the hydrolysis products of dichloromethyl-α-naphthylsilane[106]. When

the amount of alcohol is reduced by a factor of 4, the yield of disiloxane falls to 25.5% and that of trisiloxane to 4.4%, the main reaction product being $C_4H_9O[CH_3(\alpha\text{-}C_{10}H_7)SiO]_4H$ (53.3%). The corresponding 1,3-dibutoxydisiloxane was also obtained by the reaction of dichloromethyl-α-naphthylsilane with butyl alcohol (yield 11%) or with sodium butoxide (yield 5–6%). In both cases dibutoxymethyl-α-naphthylsilane is formed simultaneously in yields of 60 and 80% respectively[106]. The hydrolysis is sometimes carried out in the presence of hydrogen chloride acceptors.

$\alpha\omega$-Dimethoxyoligodimethylsiloxanes ($n = 2-6$) were isolated in 72–76% yield after partial alcoholysis of dichlorodimethylsilane and the subsequent interaction of the alkoxychlorodimethylsilane formed with $NaHCO_3$. $\alpha\omega$-Diethoxy- and $\alpha\omega$-di-isopropoxy-oligosiloxanes were obtained similarly[107,108]. $\alpha\omega$-Di-t-butoxyoligodimethylsiloxanes with $n = 1-5$ were synthesised directly by the esterification of dichlorodimethylsilane with t-butyl alcohol in the presence of pyridine[109].

$\alpha\omega$-Dialkoxyoligosiloxanes with two organic substituents per unit may be obtained by the exchange of the functional groups in the oligosiloxanes. Thus treatment of $\alpha\omega$-dichloro-oligodialkylsiloxanes with a mixture of anhydrous alcohol and pyridine in benzene leads to 1,7-diethoxyoctaethyltetrasiloxane (70%), 1,7-diethoxytetraethyltetrapropyltetrasiloxane (69%), and tetrabutyl-1,7-diethoxytetraethyltetrasiloxane (73.3%)[38].

If the formation of hydrogen chloride or its salts is undesirable, orthoformic esters may be employed instead of alcohol. The oligomers $R'O(R_2SiO)_nSiR_2OR'$ (R' = alkyl, aryl, or alkylaryl) with $n = 2-1000$ were obtained by this method[110].

$\alpha\omega$-Dialkoxyoligosiloxanes were obtained from $\alpha\omega$-dichloro-oligosiloxanes with trimethylsiloxy-groups in the main chain and CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$, and C_4H_9OH: [60,61]

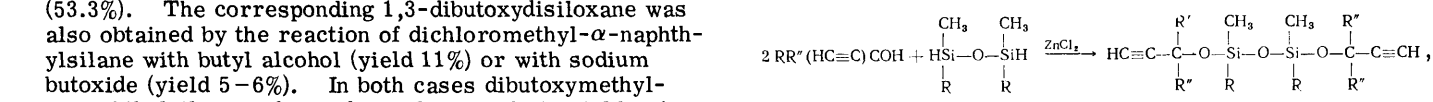
$$RO[(CH_3)_2SiO]_2SiO\{Si[OSi(CH_3)_2]_2O\}_n[OSi(CH_3)_2]_2OR \quad (n = 0,1,2,3,4)$$

and

$$RO(R')CH_3SiO\{Si[OSi(CH_3)_2]_2O\}_nSiCH_3(R')OR \quad (n = 1,2,3 \text{ etc. } R = CH_3 \text{ or } C_6H_5).$$

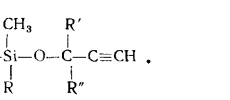
Heterofunctional condensation of dichloromethylphenylsilane with diethoxydimethylsilane, diethoxymethylphenylsilane, and diethoxyethylphenylsilane (in proportions of 1 : 2) in the presence of $FeCl_3$ leads to 1,3-diethoxy-1,1,3-trimethyl-1-phenyldisiloxane, 1,3-diethoxy-1,3-dimethyl-1,3-diphenyldisiloxane, 1,3-diethoxy-3-ethyl-1-methyl-1,3-diphenyldisiloxane, 1,5-diethoxypentamethyl-3-phenyltrisiloxane, 1,5-diethoxy-1,3,5-trimethyl-1,3,5-triphenyltrisiloxane, 1,5-diethoxy-1,5-diethyl-3-methyltriphenyltrisiloxane, 1,7-diethoxyhexamethyl-3,5-diphenyltetrasiloxane, and 1,7-diethoxy-1,3,5,7-tetramethyl-1,3,5,7-tetraphenyltetrasiloxane[111]. The redistribution of functional groups occurring in this process leads to the formation of a mixture of low-molecular-weight and high-molecular-weight condensation products, which hinders the isolation of the pure substances. Therefore the yield of tetrasiloxane does not exceed 47% and sometimes reaches only 13%. $(C_6H_5)_2Si[OSi(CH_3)_2OCH_3]_2$ was obtained by the heterofunctional condensation of diphenylsilanediol with $(CH_3)_2Si(OCH_3)Cl$.[53]

1,3-Dialkoxy-1,3-dialkyl-1,3-dimethyldisiloxanes have been synthesised by the dehydrocondensation of tertiary acetylenic alcohols with 1,3-diethyl-1,3-dimethyl- or 1,3-dimethyl-1,3-dipropyl-1,3-dihydrodisiloxanes in the presence of $ZnCl_2$ according to the mechanism[112]

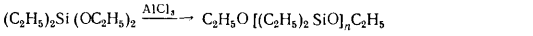


where (a) R = C_2H_5 and R' = R'' = H, (b) R = C_3H_7 and R' = R'' = H, (c) R = C_2H_5, R' = H, and R'' = C_3H_7, (d) R = C_2H_5 and R' = R'' = CH_3, (e) R = R'' = C_2H_5 and R' = CH_3, (f) R = C_3H_7, R' = CH_3, and R'' = n-C_4H_9.

Under certain reaction conditions and for certain structures of the initial components, monoalkynyloxy-derivatives of tetra-alkyldisiloxanes are also formed:



1,3-Diethoxytetraethyldisiloxane and 1,5-diethoxyhexaethyltrisiloxane were obtained by heating diethoxydiethylsiloxane in an autoclave at about 300°C in the presence of $AlCl_3$ or BCl_3:[113]

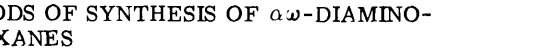


(n = 2 or 3).

$[CH_3CH = CHOSi(C_2H_5)_2]_2O$ and $[(C_2H_5)_2SiOC(CH_3) = CHCH(CH_3)_2]_2O$ were obtained by the addition of the tetraalkyldisiloxane to acrolein or mesityl oxide[114,115].

V. METHODS OF SYNTHESIS OF $\alpha\omega$-DIAMINO-OLIGOSILOXANES

$\alpha\omega$-Diamino-oligodialkyldisiloxanes are obtained by the reaction of $\alpha\omega$-dichloro-oligodialkylsiloxanes with ammonia or amines:

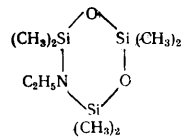


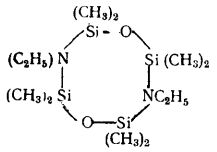
where R' = alkyl or H. Depending on the nature of the substituents at the nitrogen atom, the chain length of $\alpha\omega$-dichloro-oligosiloxanes, and the reaction conditions, $\alpha\omega$-diamino-oligosiloxanes, cyclosiloxazanes, or their mixtures may be obtained.

The initial oligomers containing up to six silicon atoms in the molecule react with an excess of ammonia to form cyclic compounds—cyclosilazanes and cyclosiloxazanes[116]. With increase of the number of silicon atoms in the chain of $\alpha\omega$-dichloro-oligosiloxanes to 7–11, the tendency by the latter towards ring formation falls and linear $\alpha\omega$-diamino-oligodialkylsiloxanes are formed.

When an ethereal solution of an $\alpha\omega$-dichloro-oligosiloxane was added to liquid ammonia, the oligomers $NH_2[(CH_3)_2SiO]_nSi(CH_3)_2-NH_2$ with $n = 6$ (72%), $n = 7$ (58.6%), $n = 8$ (46.4%), $n = 9$ (54.8%), and $n = 10$ (45.4%) were obtained. The analogous reaction with methylamine leads to 1,3-di(methylamino)tetramethyldisiloxane and 1,5-di(methylamino)-hexamethyltrisiloxane[117,118], which, in contrast to the corresponding amino-derivatives, do not cyclise on heating. When gaseous methylamine is passed into a solution of $\alpha\omega$-dichloro-oligodimethylsiloxanes, the cyclisation products $[Si(CH_3)_2OSi(CH_3)_2N(CH_3)]_2$ and $Si(CH_3)_2OSi(CH_3)_2N(CH_3)$ and the linear dimer $(CH_3)N[Si(CH_3)_2OSi(CH_3)_2N(CH_3)_2]_2$ are formed together with 1,3-di(methylamino)tetramethyldisiloxane (yield 40%) and 1,5-di(methylamino)hexamethyltrisiloxane (32%).

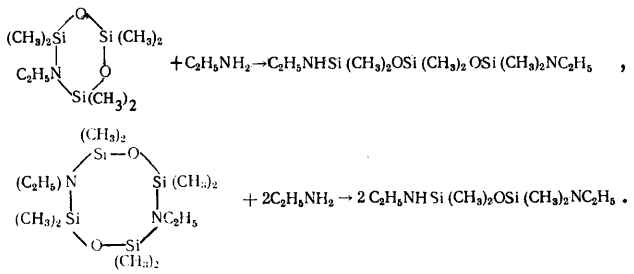
However, when the reaction is carried out at −60°C, the products are αω-di(methylamino)oligodimethylsiloxanes containing between 2 and 10 silicon atoms in yields of 51.8, 65.5, 39.8, 31.4, 21.1, 62.0, 73.3, 74.1, and 37.4% respectively[119]. Depending on the conditions, the products of the analogous reaction of methylamine may be both linear and six- and eight-membered cyclic compounds:





The latter are formed when the process is carried out in a solvent with equimolar proportions of the αω-dichloro-oligosiloxane and the amine. In the absence of a solvent and in the presence of an excess of the amine, the products are the linear oligomers $C_2H_5NH[(CH_3)_2SiO]_nSi(CH_3)_2NHC_2H_5$ with n = 1−4.[120]

It has been suggested that cyclic condensation products are formed in the initial reaction stage and undergo ring opening under the action of the excess of the amine with formation of αω-diamino-oligodimethylsiloxanes[120]:



αω-Dichloro-oligodimethylsiloxanes containing between 5 and 10 silicon atoms in the molecule form linear αω-di(ethylamino)-oligodimethylsiloxanes even in the presence of only the equimolar reactant ratio. The yields of the oligomers are 37.5% for n = 5, 30.5% for n = 6, 36.0% for n = 7, 28.6% for n = 8, 40.8% for n = 9, and 46.5% for n = 10.[121]

The reaction of αω-dichlorodimethylsiloxane with diethylamine yielded the oligomers $(C_2H_5)_2N[(CH_3)_2SiO]_nSi(CH_3)_2N(C_2H_5)_2$ with n = 2−10, which exhibit a high thermal stability. Cyclic compounds are not isolated under these conditions. The yield of the oligomers was between 30 and 60%.[121] With increase in the size of the organic substituent at the nitrogen atom, the capacity for cyclisation diminishes.

The reaction of 1,5-dichlorohexamethyltrisiloxane with n-butylamine gave 1,5-di-(n-butylamino)hexamethyltrisiloxane, which cyclises on heating only in the presence of $CuBr_2$ or $(NH_4)_2SO_4$.[54] αω-Dichloro-oligosiloxanes containing more or less than three silicon atoms in the molecule react with n-butylamine, also forming only linear αω-di(n-butylamino)oligodimethylsiloxanes with n = 1 (70.3%), n = 2 (50.2%), n = 3 (57.7%), n = 4 (50.8%), n = 5 (34.9%), n = 6 (35.8%), n = 7 (43.7%), and n = 8 (51.5%).[122]

VI. SYNTHESIS OF OLIGOSILOXANE-αω-DIOLS

1. Hydrolytic Cleavage of Cyclosiloxanes

The cleavage of oligomeric cyclosiloxanes with two organic substituents by water takes place in the presence of acid[123-125] or alkaline[126,127,129] catalysts: $(R_2SiO)_n + H_2O \xrightarrow{H^+,\ OH^-} HO(R_2SiO)_nH$. In the absence of catalysts cyclosiloxanes are cleaved by water only under severe conditions (at 250°C under pressure), which promote the formation of high-molecular-weight siloxane αω-diols[128].

Acids with a dissociation constant $>6.5 \times 10^{-2}$ (HCl, H_2SO_4, p-$CH_3C_6H_4SO_3H$) have been suggested as catalysts for the hydrolytic cleavage of siloxanes and tetrahydrofuran (THF), dimethylformamide, acetonitrile, or acetone have been proposed as solvents[123].

Thus when D_3 is cleaved with 0.05 N HCl in tetrahydrofuran, the products are about 82% of hexamethyltrisiloxane-1,5-diol, about 13% of the initial cyclosiloxane, and about 6% of an unidentified compound. Hexaphenylcyclotrisiloxane is cleaved with 0.5 N HCl in acetone to hexaphenyltrisiloxane-1,5-diol in yields up to 34%.

1,3-Dimethyl-1,3-diphenyldisiloxane-1,3-diol is obtained by the cleavage of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane with an excess of potassium hydroxide in alcoholic solution with subsequent hydrolysis of the resulting siloxanolate in the presence of KH_2PO_4.[126] The yield of siloxanediol was 87%.

Ammonia and amines are also used as catalysts for the hydrolytic cleavage of cyclotrisiloxanes with six organic substituents[129]. In this case the rearrangement of siloxane bonds, observed in catalysis by strong acids or bases, is ruled out. Such catalysts make it possible to obtain virtually pure linearoligosiloxane-αω-diols with two organic substituents per unit. For example, the cleavage of 1,3,5-tri-(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane with a mixture of 29% ammonia solution, water, and acetone over a period of 16 h at 20°C gave mainly $HO[CH_3(CF_3CH_2CH_2)SiO]_3H$.

Acid and basic ion-exchange resins are also used as catalysts for the hydrolytic cleavage of cyclosiloxanes[130,131]. Thus in the presence of Amberlite IR-120, D_3 dissolved in acetone is converted into $HO[(CH_3)_2SiO]_nH$ with n = 3 (41%) and n = 6 (11.2%). Basic resins promote the formation of a hexamer[131].

Octamethyltetrasiloxane-1,7-diol was obtained by heating (150°C, 1,5 h) D_4 with 1% of glycerol and 0.5% of bleaching earth containing minerals of the montmorillonite group[132].

Oligosiloxane-αω-diols with two organic substituents per unit are also formed when cyclosiloxanes are cleaved with diphenylsilanediol[133] or with siloxane-αω-diols[126]: $(R_2SiO)_n + HO(R'_2SiO)_mH \rightarrow HO(R_2SiO)_n(R_2SiO)_mH$.

2. Hydrolysis of Silane with two Functional Groups at the Silicon Atom and Two Organic Substituents

A convenient method for the preparation of oligosiloxane-αω-diols is based on the capacity of Si−Cl, Si−OCOR, Si−OR, Si−NRR′, Si−H, Si−SH, Si−SR, etc. bonds in the corresponding disubstituted silanes with two organic groups and in αω-difunctional oligosiloxanes to be readily cleaved by water with formation of Si−OH bonds. Depending on the hydrolysis conditions, the latter can persist or condense further: $nR_2SiX_2 + (n+1)H_2O \rightarrow HO(R_2SiO)_nH + 2nHX$ (X = Cl, OCOR, OR, NRR′, H, SH, or SR).

The reactivity (including the reactivity with respect to water) of Si–X bonds in compounds with functional groups at the silicon atoms falls in the following sequence: Cl > OCOR > OR.[6] Usually the most readily available dichlorosilanes with two organic substituents are hydrolysed. However, during their hydrolysis hydrochloric acid appears in the reaction medium and causes the cyclisation of the siloxanediols. To avoid the formation of a large amount of cyclosiloxanes and high-molecular-weight siloxanediols, the hydrolysis is usually performed under mild conditions (at a low temperature and in the presence of a hydrogen chloride acceptor). The first member of the homologous series of the $HO[(CH_3)_2SiO]_nH$ ($n \geq 2$) oligomers—tetramethyldisiloxane-1,3-diol—was synthesised in a yield of up to 60% by the hydrolysis of dichlorodimethylsilane with a large excess of cold water (2°C) in the presence of NH_4OH (pH ~ 7) [134,135]. When gaseous ammonia is introduced, reproducible results are not always obtained owing to the difficulty of regulating the rate of its supply and the removal of the heat evolved.

Hydrogen chloride can also be neutralised by ammonium sulphate containing magnesium carbonate[136], $NH_4HCO_3(NH_4)_2CO_3$,[138] $NaHCO_3$, $Na_2B_4O_7.10H_2O$,[137] or ammonium bicarbonate carbamate ($NH_4HCO_3.NH_2CO_2NH_4$).[138] In the latter case a pH of 6–8 can be readily attained during the hydrolysis. However, the yield of tetramethyldisiloxane-1,3-diol is only 39%. A decrease of the amount of water leads to a shift of the pH of the reaction medium to the weakly acid region, which makes it possible to obtain higher oligosiloxanediols (hexamethyltrisiloxane-1,5-diol and decamethylpentasiloxane-1,9-diol).

Tetraphenyldisiloxane-1,3-diol (51%) and hexaphenyltrisiloxane-1,5-diol (18%) were obtained by the same method from dichlorodiphenylsilane. The hydrolysis of $(C_6H_5)_2SiCl_2$ with cold water gives low yields of tetraphenyldisiloxane-1,3-diol and hexaphenyltrisiloxane-1,5-diol[139]. Tetraphenyldisiloxane-1,3-diol was also obtained by the hydrolysis of $(C_6H_5)_2SiCl_2$ after which the resulting $(C_6H_5)_2Si(OH)_2$ was allowed to stand in the solvent (benzene–petroleum ether) for three days[140]. Tetramethyldisiloxane-1,3-diol is formed in a very low yield when dichlorodimethylsilane is treated with aqueous t-butyl alcohol[109].

Acid hydrolysis of dichloromethylphenylsilane results in the formation of only cyclotrisiloxanes with *cis*- and *trans*-structures[141]. On the other hand, hydrolysis in dilute ethereal solutions by aqueous alkalis yields ethylphenylsilanediol and 1,3-dimethyl-1,3-diphenyldisiloxane-1,3-diol[142].

Siloxanediols containing complex aromatic and alkyl groups at the silicon atoms have been obtained by the hydrolysis of more complicated dialkyl-, alkylaryl-, or diaryl-chlorosilanes. In this case the hydrolysis of the Si–Cl bond is difficult owing to the steric effect of the substituents at the silicon atoms. The silanediol formed in the first stage of the hydrolysis may be isolated from the reaction mixture. In order to synthesise silanediols, the reaction mixture sometimes has to be heated. Thus in the preparation of deca-*p*-tolylpentasiloxane-1,5-diol, dichlorodi-*p*-tolylsilane is hydrolysed by a mixture of water and ether, after which the ether is removed and the mixture heated to 250°C (at 1 mmHg pressure) and again hydrolysed[143]. The hydrolysis of $(p\text{-}ClC_6H_4)_2SiCl_2$ in toluene, ether, or isopentyl alcohol gives mainly tetra-(*p*-chlorophenyl)disiloxane-1,3-diol. When aqueous alkali or ammonia is employed, a mixture of di-(*p*-chlorophenyl)silanediol and tetra-(*p*-chlorophenyl)disiloxane-1,3-diol is formed. In ethereal solution only the monomeric silanediol is produced and on heating to 110°C is converted into hexa-(*p*-chlorophenyl)trisiloxane-1,5-diol.[144]

Dichloromethyl-α-naphthylsilane is hydrolysed to methyl-α-naphthylsilanediol and its low-molecular-weight condensation products $HO[CH_3-(\alpha-C_{10}H_7)SiO]_nH$.[106] Oligomers with three and four silicon atoms in the molecule have been isolated from the condensation products of ethylphenyl- and benzylethyl-silanediols[145,146].

The study of the effect of bulky alkyl groups (n-hexyl, n-octyl, iso-octyl, and isononyl) at the silicon atoms on the nature of the hydrolysis products of the corresponding dialkyldichlorosilanes[147] showed that in 34.7% hydrochloric acid only cyclic condensation products are formed. In dilute hydrochloric acid a mixture of cyclic and linear siloxanes was obtained, from which 1,3-diethyl-1,3-diiso-octyldisiloxane-1,3-diol (up to 58%), 1,3,5,7-tetraethyl-1,3,5,7-tetraiso-octyltetrasiloxane-1,7-diol (20%), and 1,3,5,7-tetrahexyl-1,3,5,7-tetramethyltetrasiloxane-1,7-diol (12.3%) were isolated.

Prolonged heating of silanediols with two organic substituents, particularly in the presence of dehydrating agents, promotes the successive formation of dimeric, trimeric, and higher oligomeric siloxane-αω-diols. The reaction takes place in steps. By altering the condensation conditions, it is possible to achieve the preferential formation of oligosiloxane-αω-diols, siloxanediols, or cyclosiloxanes[142].

Monomeric compounds R_2SiX_2 containing other functional groups X, for example X = OCOR or OR, are also used for the synthesis of oligosiloxane-α-diols. Thus di(methylvinyl)-, di(allylmethyl)-, di(phenylvinyl), di(chlorophenylvinyl), and di(allylphenyl)-siloxane-1,3-diols have been obtained in yields up to 90–98% by the hydrolysis of the corresponding diacetoxysilanes with two organic substituents[148,149].

Dimethyldi-(1-pentynyl)disiloxane-1,3-diol and di-(1-hexynyl)dimethyldisiloxane-1,3-diol were prepared by the hydrolysis of the corresponding diacetoxydialkynylsilanes with a saturated solution of sodium chloride[150,151]. The cyclosiloxane $[CH_3(CH_2)_3C \equiv CSiO]_4$ is formed at the same time, its yield increasing with temperature and the rate of addition of the acetoxysilane. The hydrolysis of alkoxysilanes with two other organic substituents is usually carried out in the presence of acid catalysts. Thus by hydrolysing diethoxyphenylvinylsilane with 0.1 *N* HCl in ethanol, 1,3-diphenyl-1,3-divinyldisiloxane-1,3-diol was obtained[152], while diethoxydiethylsilane (in 15% HCl) gave tetraethyldisiloxane-1,3-diol (yield up to 88%).[153–155]

Hydrolysis of diethoxydimethylsilane in the presence of traces of sulphuric acid resulted in the formation of tetramethyldisiloxane-1,3-diol (yield up to 66%).[156] The same compound has been obtained by the hydrolysis of dimethoxydimethylsilane[157].

Oligosiloxanediols containing pentafluorophenyl groups at the silicon atoms, $HO[(CH_3(C_6F_5)SiO]_nH$ ($n = 2$ or 4), have been obtained in 80–90% yield by the hydrolysis of dialkoxymethyl(pentafluorophenyl)silane in an alcoholic medium in the presence of acetic acid[158]. Tetramethyldisiloxane-1,3-diol is formed in the hydrolysis of hexamethylcyclotrisilthiane $[(CH_3)_2SiS]_3$ in the presence of sodium hydroxide[159]:

$$2\,[(CH_3)_2SiS]_3 + 12\,NaOH \rightarrow 3HO\,[(CH_3)_2SiO]_2H + 6Na_2S + 3H_2O\ .$$

the same compound has been obtained by the decomposition of an ethereal solution of sodium dimethylsilanediolate

with acetic acid[160,161] or with carbon dioxide[162] and also by keeping a solution of $(CH_3)_2Si(OH)_2$ in 0.001 *N* aqueous acetic acid[163].

Oligosiloxane-$\alpha\omega$-diols are formed in the hydrolysis of the corresponding hydrosilanes and hydrosiloxanes in the presence of silver, Ag_2O, CuO,[164] and ruthenium on charcoal[165] or when oxygen is passed through a mixture containing a hydrosiloxane, an amine, and a copper(I) salt[166]:

$$H(R_2SiO)_nSiR_2H + H_2O \xrightarrow{Ag,Ag_2O,Ru/C} HO(R_2SiO)_nSiR_2OH + H_2\ (n=0,1\ \text{etc.}),$$

$$H(R_2SiO)_nSiR_2H + O_2 \xrightarrow[CuX]{R_3N} HO(R_2SiO)_nSiR_2OH.$$

3. Hydrolysis of Terminal Functional Groups

The easiest method of synthesising pure oligosiloxane-$\alpha\omega$-diols with two organic substituents is based on the hydrolysis of the terminal functional groups in the corresponding $\alpha\omega$-disubstituted oligosiloxanes with two organic substituents:

$$X(R_2SiO)_{n-1}SiR_2X + 2H_2O \rightarrow HO(R_2SiO)_nH + 2HX\ (X=Cl, OR, OCOR\ \text{etc.}).$$

The disadvantages of the method are the necessity for a preliminary synthesis of the initial oligosiloxane and the possibility (under unfavourable reaction conditions) of side processes involving condensation (primarily cyclisation), cleavage, and rearrangement of the siloxane bonds. The effect of the conditions in the hydrolysis of $\alpha\omega$-dichloro-oligodimethylsiloxanes on the composition of the hydrolysis products has been investigated in fair detail[6,167]. Oligodimethylsiloxane-$\alpha\omega$-diols $HO[(CH_3)_2SiO]_nH$ have been obtained in high yields [$n = 2$ (88%), $n = 3$ (74%), $n = 4$ (76%), and $n = 5$ (55%)] by adding rapidly an approximately 10% etheral solution of the corresponding $\alpha\omega$-dichloro-oligodimethylsiloxane to a 5% solution of sodium hydroxide.

As in the case of dichlorodimethylsilane, hydrolysis in an acid medium leads to a mixture of linear (50%) and cyclic (50%) siloxanes. The only exception is 1,5-dichlorohexamethyltrisiloxane which yields 12% of cyclosiloxanes. By hydrolysing the corresponding $\alpha\omega$-dichloro-oligosiloxanes containing two organic substituents with a 5% solution of alkali in ether, oligodimethylsiloxane-$\alpha\omega$-diols, containing between two and nine silicon atoms in the molecule[168], oligomethylphenylsiloxane-$\alpha\omega$-diols with $n = 2-4$ [169], and also pentaethyltripropyl-, tetraethyltetrapropyl, and tetrabutyltetraethyl-tetrasiloxane-1,7-diols were obtained in yields up to 88%.[38]

When $NaHCO_3$, Na_2CO_3, and NH_4OH were used as neutralising agents, oligodimethylsiloxane-$\alpha\omega$-diols with $n = 9$ (70.9%), $n = 13$ (88.9%), and $n = 53$ (66.5%),[170] siloxanediols containing fluorinated groups at the silicon atoms $HO[CH_3(RCH_2CH_2)SiO]_nH$ (R = perfluoroalkyl containing between one and three carbon atoms; $n = 2$, 3, or 4) [171], and also the siloxanediols $RR'Si[OSi(R''R''')OH]_2$ [$R = R' = CH_3$, $R'' = R''' = C_6H_5$; R = cyclo-C_6H_{11}, $R' = CH_3$, $R'' = CH_2C \equiv CCH_3$, $R''' = CH_3$; $R'' = R''' = CH_3$, $R = C_6H_5$, $R' = CH_3$; $R'' = R''' = CH_3$, $R = C_6H_5$, $R' = CH{=}CH_2$; $R'' = R''' = CH_3$, $R = C_2H_5$, $R' = CH_3$; $R'' = R''' = CH_3$, $R = CH_2CH(CH_3)C_6H_5$, $R' = CH_3$; $R'' = R''' = CH_3$, $R = CH_2CH_2CF_3$, $R' = CH_3$; $R'' = R''' = CH_3$, $R = C_{18}H_{37}$, $R' = CH_3$; $R'' = R''' = CH_3$, R = chlorocyclohexyl, $R' = CH_3$] [53], and oligomers in which the main chain is bounded by trimethylsiloxy-groups were obtained[58,59]:

$$HO[(CH_3)_3SiO]_2SiO\{Si[OSi(CH_3)]_2O\}_nSi[OSi(CH_3)_2]_2OH$$

and

$$HO(R)CH_3SiO\{Si[OSi(CH_3)_3]_2O\}_nSiCH_3(R)OH\ (R=CH_3, C_6H_5;\ n=1, 2, 3, \text{etc.})$$

1-Methyl-1,3,3-triphenyldisiloxane-1,3-diol may be obtained by the hydrolysis of 1,3-dichloro-1-methyl-1,3,3-triphenyldisiloxane in the presence of aniline[16]. Hydrolysis of an ethereal solution of 1,3-dichlorotetraphenyldisiloxane and 1,5-dichlorohexaphenyltrisiloxane in an aqueous dioxan medium (molar ratio dichlorosiloxane: water = 2.1 or 1.5 : 1) yields tetraphenyldisiloxane-1,3-diol (92%) and hexaphenyltrisiloxane-1,5-diol (64%) [19].

Two stereoisomers [meso- and (±)-forms] of 1,3-dimethyl-1,3-diphenyldisiloxane-1,3-diol were obtained by the hydrolysis of a diastereoisomeric mixture of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane with 10% aqueous ammonia in ether[15].

Oligosiloxane-$\alpha\omega$-diols with two organic substituents can also be obtained by the hydrolysis of the corresponding $\alpha\omega$-dialkoxyoligosiloxanes with two organic substituents per unit. However, their hydrolysis is much slower than that of the corresponding $\alpha\omega$-dichloro-oligosiloxanes with two organic substituents per unit and in many cases requires the use of acid and basic catalysts. For example, tetraphenyldisiloxane-1,3-diol is formed on hydrolysis of ethoxytetraphenyldisiloxane with 8% hydrochloric acid in toluene or pentyl alcohol[105]. However, oligodimethylsiloxane-$\alpha\omega$-diols with $n = 1-5$ has been obtained by the hydrolysis of $\alpha\omega$-diethoxyoligodimethylsiloxanes in a neutral medium[172].

$\alpha\omega$-Diacetoxyoligosiloxanes with two organic substituents per unit can be used to synthesise siloxanediols[173,174]. They are more reactive than alkoxyoligosiloxanes and form on hydrolysis acetic acid, which does not exhibit a powerful condensing activity like that of hydrogen chloride liberated on hydrolysis of $\alpha\omega$-dichloro-oligosiloxanes. While the hydrolysis of the latter must be carried out under very mild conditions (tenfold dilution of the oligomers with the solvent and the use of a hydrogen chloride acceptor), $\alpha\omega$-diacetoxysiloxanes can be hydrolysed in the absence of solvents and in the absence of an acetic acid acceptor. However, in some cases hydrolysis in the presence of $CaCO_3$ proceeds more smoothly. $HO[(CH_3)_2SiO]_nH$ with $n = 2-5$ (yield 60–90%) and $HO[CH_3(CF_3CH_2CH_2)SiO]_nH$ with $n = 2-4$ (yield 60–80%) have been obtained.

In the hydrolysis of $\alpha\omega$-diacetoxydimethyloligosiloxanes in the presence of CH_3COOH acceptors ($CaCO_3$, NH_4HCO_3, NH_4OH) the highest yields are achieved when $CaCO_3$ is employed. With increase of the basicity of the CH_3COOH acceptor, the cyclosiloxanes D_3 and D_4 appear in the hydrolysis products.

In contrast to $\alpha\omega$-diacetoxydimethylsiloxanes, $\alpha\omega$-diacetoxyoligo-(3,3,3-trifluoropropyl)methylsiloxanes are converted more smoothly into the corresponding siloxanediols when stronger bases, for example sodium hydroxide, are employed as CH_3COOH acceptors. This is evidently associated with the steric effect of the 3,3,3-trifluoropropyl groups, which prevent the condensation of the siloxanediol formed and at the same time hinder the hydrolysis of the acetoxy-groups.

The hydrolysis of $C_6H_5RSi[OSiR'R''(OAc)]_2$ ($R = C_6H_5$, $R' = R'' = CH_3$; $R = CH_3$, $R' = R'' = C_6H_5$; $R = C_6H_5$, $R' = C_6H_5$, $R'' = CH_3$) in ethereal solution in the presence of sodium carbonate has been described[53].

4. The Anhydrocondensation Reaction

Oligosiloxane-$\alpha\omega$-diols with two organic substituents per unit are formed in the anhydrocondensation of silanediols with two organic substituents[175,176]: $n R_2Si(OH)_2 \rightarrow HO(R_2SiO)_nH + (n-1)H_2O$, or in the anhydrocondensation of lower oligodialkylsiloxane-$\alpha\omega$-diols:

$$HO(R_2SiO)_nH + HO(R'_2SiO)_nH \rightarrow HO(R_2SiO)_n(R'_2SiO)H + H_2O.$$

For example, in the thermal condensation of diphenylsilanediol, hexaphenyltrisiloxane-1,5-diol was isolated[175]. On heating to 200°C, hexamethyltrisiloxane-3,3-diol is converted into the corresponding di- and tri-siloxane-$\alpha\omega$-diols in which the silicon atoms in the main chain are linked to trimethylsiloxy-groups[176]:

$$[(CH_3)_3SiO]_2Si(OH)_2 \rightarrow HO\{[(CH_3)_2SiO]_2SiO\}_nH \quad (n=2 \text{ or } 3)$$

VII. PREPARATION OF DISODIUM SALTS OF OLIGOSILOXANE-$\alpha\omega$-DIOLS

Disodium (or dipotassium salts) of oligosiloxane-$\alpha\omega$-diols with two organic substituents per unit are readily obtained by the cleavage of siloxanes containing two organic substituents with sodium (or potassium) hydroxide: $(R_2SiO)_n + 2MOH \rightarrow MO(R_2SiO)_nM + H_2O$ (M = Na or K). They are usually formed in as hydrates containing between two and five water molecules, which can be removed by heating in a vacuum.

As early as 1914,[161] salts containing as many silicon atoms in the molecule as the initial cyclosiloxane were obtained by the cleavage of hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane with 3% solutions of sodium hydroxide or potassium hydroxide. When the product of the hydrolysis of dichlorodimethylsilane was cleaved with approximately 50% aqueous sodium hydroxide, disodium salts of tetramethyldisiloxane-1,3-diol and octamethyltetrasiloxane-1,7-diol were obtained[177]. Such reactions are usually carried out in the presence of alcohol. Thus, by cleaving the corresponding cyclosiloxanes with sodium hydroxide in methanol, the salts $NaO[(CH_3)_2SiO]_2Na.5H_2O$, $NaO[CH_3(C_6H_5)SiO]_3Na.4H_2O$,[178] and also the anhydrous salts $NaO[(CH_3)_2SiO]_2Na$, $NaO[CH_3(C_6H_5)SiO]_2Na$,[179] $NaO[CH_3(C_6H_5)SiO]_nNa$ (n = 1, 2, or 3),[180] and $NaO[CH_3(C_6H_5)SiO]_nNa$ (n = 4, 8, 12, etc.)[181] were obtained. The highest yield of the salts of oligomethylphenyl- and oligoethylphenyl-siloxane-$\alpha\omega$-diols was attained by cleaving the corresponding cyclosiloxanes with a solution of sodium hydroxide in 50% aqueous ethanol[182]. The alkali metal hydroxide may be replaced by the metal oxide[182].

The cleavage of cyclosiloxanes with sodium hydroxide is reversible[179]: $(R_2SiO)_3 + NaOH \rightleftharpoons HO(R_2SiO)_3Na \rightleftharpoons NaO(R_2SiO)_3Na + H_2O$; $2HO(R_2SiO)_3Na \rightarrow NaO(R_2SiO)_6Na + H_2O$. Therefore the reaction mixture contains salts with different chain lengths, which, however, largely correspond to the amount of alkali taken and the ring size. Regardless of the proportions of the initial reactants in the alkaline cleavage of cyclosiloxanes one of the products is always the sodium salt of tetramethyldisiloxane-1,3-diol, the yield of which falls as the molar ratio NaOH : cyclosiloxane decreases[183].

Disodium salts of siloxane-$\alpha\omega$-diols with longer chain lengths can be obtained by reducing the amount of sodium hydroxide used to cleave the cyclosiloxane, which leads to the parallel occurrence of the anhydrocondensation process

$$2(R_2SiO)_n + NaOH \rightarrow 2NaO(R_2SiO)_nH \xrightarrow{-H_2O} NaO(R_2SiO)_{2n}Na$$

or the cross-linking of the low-molecular-weight oligomers by dichlorodimethylsilane[184]: $(CH_3)_2SiCl_2 + 2NaO(R_2SiO)_nNa \rightarrow (CH_3)_2Si[O(R_2SiO)_nNa]_2 + 2NaCl$. Salts containing various substituents at the silicon atoms may be obtained by the last method.

Owing to their acid properties, due to the $p_\pi - d_\pi$ interaction between the p electrons of oxygen and the $3d$ orbitals of silicon, siloxanediols can react with alkali metals, forming the corresponding salts: $HO(SiR_2O)_nH + 2M \rightarrow MO(SiR_2O)_nM + H_2$. By allowing tetra-alkyldisiloxane-1,3-diols to react with metallic sodium in xylene[153] or in liquid ammonia[185], the corresponding salts of the diols were synthesised.

The reaction with lithium proceeds similarly[186]. Magnesium and aluminium also react readily with siloxanediols, forming polyalkylmetallosiloxanes[153,187].

REFERENCES

1. R. J. H. Voorhoeve, "Organohalosilanes, Precursors to Silicones", Amsterdam, 1967; C. Eaborn and R. W. Bott, in "Organometallic Compounds of the Group IV Elements" (Edited by A. G. MacDiarmid), New York, 1969, pp. 188–213.
2. S. A. Golubtsov, Doctoral Thesis, Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, 1963.
3. J. J. Zuckermann, Annalen Inorg. Radiochem., 6, 383 (1964).
4. S. I. Sadykh-Zade and A. D. Petrov, Trudy Inst. Khim. Akad. Nauk Azerb. SSR, 18, 107 (1960).
5. A. D. Petrov, V. F. Mironov, V. A. Ponomarenko, and E. A. Chernyshev, "Sintez Kremniiorganicheskikh Monomerov" (Synthesis of Organosilicon Monomers), Izd. Akad. Nauk SSSR, Moscow, 1961, pp. 35–75.
6. N. N. Sokolov, "Metody Sinteza Polyorganosiloksanov" (Methods of Synthesis of Polyorganosiloxanes), Gosenergoizdat, Moscow, 1958.
7. K. A. Andrianov and N. N. Sokolov, Dokl. Akad. Nauk SSSR, 101, 81 (1955).
8. E. G. Rochow and W. F. Gilliam, J. Amer. Chem. Soc., 63, 798 (1941).
9. W. J. Patnode, US P. 2 381 366 (1945); Chem. Abs., 39, 4890 (1945); B. P. 631 018 (1948); Chem. Abs., 44, 4492 (1950).
10. W. J. Patnode and D. F. Wilcock, J. Amer. Chem. Soc., 68, 358 (1946).
11. G. Greber and L. Metzinger, Makromol. Chem., 39, 167 (1960).
12. H. Baba and S. Nishizaki, Japanese P. 1444 (1957); Chem. Abs., 52, 4679 (1958).
13. H. Manami, S. Nishizaki, and Nippon Kagaku Zasshi, J. Chem. Soc. Japan., 79, 60 (1958); Chem. Abs., 54, 5436 (1960).
14. J. F. Hyde and P. Z. Brown, US P. 2 902 507 (1959); Chem. Abs., 54, 5467b (1960).
15. W. H. Daudt and J. F. Hyde, J. Amer. Chem. Soc., 74, 386 (1952).
16. T. G. Selin, French P. 1 374 653 (1962); Chem. Abs., 62, 6513 (1965).
17. K. A. Andrianov, V. E. Nikitenkov, L. A. Kukharchuk, and N. N. Sokolov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1004 (1958).
18. J. G. Murray, F. F. Holub, and M. J. Smith, US P. 3 125 632 (1962); Chem. Abs., 61, 4394 (1964).

19. C. H. Burkhard, J. Amer. Chem. Soc., 67, 2173 (1945).
20. V. Bažant and J. Benes, Chem. Listy, 52, 1757 (1958).
21. P. L. Brown, US P. 2 911 427 (1959); B. P. 844 279 (1959); Chem. Abs., 54, 5467c (1960).
22. S. Chrzczonowicz and J. Chojnowski, quoted after V. Bažant, V. Chvalovsky, and J. Rathóusky, "Organosilicon Compounds", Prague, 1965, Vol. I, p. 494, vol. II (2), p. 495.
23. J. M. Nielsen, French P. 1 440 923 (1964); Chem. Abs., 66, 19 070 (1967).
24. L. H. Shaffer and E. M. Flanigen, J. Phys. Chem., 61, 1591 (1957).
25. M. G. Voronkov and Yu. I. Skorik, Izv. Akad. Nauk SSSR, Ser. Khim., 1215 (1964).
26. K. A. Andrianov, S. A. Golubtsov, and N. N. Sokolov, Vysokomol. Soed., 1 (1952).
27. K. A. Andrianov and V. V. Severnyi, Dokl. Akad. Nauk SSSR, 134, 1347 (1960).
28. K. A. Andrianov and V. V. Severnyi, J. Organomet. Chem., 1, 268, 340 (1964).
29. V. V. Severnyi, Candidate's Thesis, Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow, 1962.
30. K. A. Andrianov and V. V. Severnyi, USSR P. 136 370 (1960); Byull. Izobret., No. 5, 25 (1961).
31. K. A. Andrianov, V. V. Severnyi, and B. G. Zavin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1456 (1961).
32. K. A. Andrianov and V. V. Severnyi, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2133 (1962).
33. K. A. Andrianov and V. V. Severnyi, Symposium, "Sintezi Svoistva Monomerov, Trudy XII Konferentsii po Vysokomolekulyarnym Soedineniyam, Baku" (Synthesis and Properties of Monomers. Proceedings of the Twelfth Conference on Macromolecular Compounds, Baku), Izd. Nauka, Moscow, 1962, p. 160.
34. K. A. Andrianov and V. V. Severnyi, Izv. Akad. Nauk SSSR, Ser. Khim., 1268 (1964).
35. K. A. Andrianov and V. V. Severnyi, Dokl. Akad. Nauk SSSR, 146, 601 (1962).
36. K. A. Andrianov and V. V. Severnyi, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1237 (1962).
37. K. A. Andrianov, V. V. Astakhin, M. O. Melikyan, N. G. Mushegyan, and V. K. Pyzhov, Zhur. Obshch. Khim., 36, 1850 (1966).
38. K. A. Andrianov, V. V. Astakhin, M. O. Melikyan, N. G. Mushegyan, and V. K. Pyzhov, Arm. Khim. Zhur., 21, 317 (1968).
39. K. A. Andrianov and V. V. Severnyi, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1788 (1961).
40. H. Niebergall, BRD P. 1 157 614 (1963); Chem. Abs., 61, 3148 (1964).
41. R. O. Sauer, US P. 2 421 653 (1947); Chem. Abs., 41, 5544 (1947); B. P. 597 178 (1948); Chem. Abs., 42, 4602 (1948).
42. K. A. Andrianov and V. V. Severnyi, Izv. Akad. Nauk SSSR, Ser. Khim., 1271 (1964).
43. V. A. Ponomarenko and N. M. Khomutova, 2122 (1966).
44. R. Anderson and T. A. Robinson, B. P. 1 040 147 (1963); Chem. Abs., 65, 20 249 (1966),
45. M. G. Voronkov and L. M. Chudesova, Zhur. Obshch. Khim., 29, 1534 (1959); Khim. i Prakt. Primenenie Kremneorg. Soed., 1, 134 (1958).
46. A. A. Zhdanov, K. A. Andrianov, and A. A. Bogdanova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1261 (1961).
47. J. E. Hyde, US P. 2 645 654 (1953); Chem. Abs., 48, 7050 (1954).
48. K. A. Andrianov, G. A. Kurakov, V. M. Kopylov, and L. M. Khananashvili, Zhur. Obshch. Khim., 36, 105 (1966).
49. P. A. McCusker and T. Ostdick, J. Amer. Chem. Soc., 81, 5550 (1959).
50. P. A. McCusker and T. Ostdick, J. Amer. Chem. Soc., 80, 1103 (1958).
51. B. A. Ashby, B. P. 990 657 (1963); BRD P. 1 217 953 (1963); Chem. Abs., 63, 3076 (1965).
52. K. A. Andrianov and N. N. Sokolov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 806 (1957).
53. R. H. Leitheiser, BRD P. 1 157 611 (1961); US P. 3 122 579 (1960); Chem. Abs., 63, 3076 (1965).
54. J. G. Murray and R. K. Griffith, J. Org. Chem., 29, 1215 (1964).
55. E. Frainnet, R. Calas, and C. Fritsch, Bull. Soc. chim. France, 1480 (1960).
56. K. A. Andrianov, L. I. Khananashvili En-Tsê Han, and V. S. Tikhonov, Zhur. Obshch. Khim., 32, 3951 (1962).
57. J. H. Hyde, US P. 2 629 726 (1950); Chem. Abs., 47, 5720 (1953).
58. C. Shaw, W. E. Smith, and H. G. Emblem, US P. 2 580 852 (1952); Chem. Abs., 46, 3327 (1952).
59. R. L. Elliott and L. W. Breed, Inorg. Chem., 4, 1455 (1965).
60. J. R. Hahn and C. W. Lentz, French P. 1 400 265 (1963); US P. 3 308 148 (1963); Bull. off propr. ind., 6, 21, 6768 (1965).
61. C. W. Lentz, French P. 1 400 263 (1963); US P. 3 308 145 (1963); Bull. off. propr. ind., 6, 21, 6767 (1965).
62. D. Bailey and T. M. O'Connor, B. P. 858 128 (1956); US P. 2 910 496 (1959); BRD P. 1 039 516 (1959); Chem. Abs., 54, 7561 (1960).
63. B. N. Dolgov, V. P. Davydova, and M. G. Voronk[illegible], Zhur. Obshch. Khim., 27, 1593 (1957).
64. S. N. Borisov and N. G. Sviridova, USSR P. 176 893 (1964); Byul. Izobret., No. 20, 20 (196[illegible]).
65. S. N. Borisov and N. G. Sviridova, J. O[illegible]nomet. Chem., 11, 27 (1968).
66. S. N. Borisov, N. G. Sviridova, and M. G. Voronkov, Zhur. Obshch. Khim., 38, 2794 (1968).
67. S. N. Borisov and N. G. Sviridova, USSR P. 210 366 (1966); Byul. Izobret., No. 6, 71 (1968).
68. S. N. Borisov and N. G. Sviridova, USSR P. 233 913 (1967); Byull. Izobret., No. 3, 80 (1969).
69. M. G. Voronkov, N. G. Sviridova, Yu. A. Yuzhelevskii, and S. N. Borisov, Zhur. Obshch. Khim., 39, 564 (1969).
70. M. O. Melikyan and D. A. Tergazarova, Arm. Khim., Zhur., 22, 82 (1969).
71. L. B. Bruner, US P. 3 032 532 (1952); B. P. 899 939 (1959); BRD P. 1 257 432 (1959); Chem. Abs., 57, 11 236 (1959).
72. A. L. Klebanskii, N. L. Kopnova, and V. S. Chugunov, USSR P. 191 801 (1965); Byull. Izobret., No. 4, 105 (1967).
73. M. G. Voronkov, Doctoral Thesis, Institute of Petrochemical Synthesis, Moscow, 1961.
74. K. A. Andrianov, A. A. Zhdanov, and S. A. Pavlov, Dokl. Akad. Nauk SSSR, 102, 85 (1955).
75. M. G. Voronkov and N. G. Sviridova, Zhur. Obshch. Khim., 40, 90 (1970).
76. M. G. Voronkov, N. G. Sviridova, I. B. Klimenko, N. G. Shchelkunov, and V. N. Churmaeva, Zhur. Obshch. Khim., 39, 2502 (1969).
77. G. H. Omietanski and W. M. Reid, US P. 3 346 610 (1963); Belgian P. 651 371 (1965); Dutch P. 6 409 022

(1965); French P. 1 411 204; BRD P. 1 218 466; Chem. Abs., 63, 11 615 (1965).
78. S. N. Borisov and N. G. Sviridova, USSR P. 220 502 (1966); Byull. Izobret., No. 20, 69 (1968).
79. S. N. Borisov, M. G. Voronkov, and N. G. Sviridova, Zhur. Obshch. Khim., 39, 559 (1969).
80. K. A. Andrianov and A. K. Dabagova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1767 (1959).
81. L. M. Volkova, K. A. Andrianov, and M. S. Obusheva, Izv. Akad. Nauk SSSR, Ser. Khim., 1986 (1963).
82. K. A. Andrianov, M. I. Klimova, L. I. Khananashvili, and M. A. Sipyagina, Izv. Akad. Nauk SSSR, Ser. Khim., 651 (1963).
83. S. Nitzsche, M. Wick, and E. Wahlfarth, BRD P. 1 167 020 (1962); Chem. Abs., 61, 9643 (1964).
84. T. Goldschmidt, French P. 1 423 531 (1964); B. P. 1 033 259 (1964); Chem. Abs., 65, 13 846 (1966).
85. L. B. Bruner, B. P. 899 938 (1959).
86. M. M. Sprung and F. O. Guenther, J. Org. Chem., 26, 552 (1961).
87. A. G. Kuznetsova, V. I. Ivanov, and S. A. Golubtsov, USSR P. 202 952 (1966); Byull. Izobret., No. 20, 38 (1967).
88. A. G. Kuznetsova, V. I. Ivanov, and S. A. Golubtsov, Zhur. Obshch. Khim., 40, 706 (1970).
89. P. L. Brown and J. F. Hyde, US P. 3 146 251 (1961); B. P. 959 144; French P. 1 327 545 (1963); Chem. Abs., 60, 553 (1964).
90. M. G. Voronkov and Z. I. Shabarova, Zhur. Obshch. Khim., 29, 1528 (1959).
91. K. A. Andrianov, Sh. V. Pichkhadze, and V. V. Komarov, Izv. Akad. Nauk SSSR, Ser. Khim., 724 (1962).
92. M. G. Voronkov, Zhur. Obshch. Khim., 29, 907 (1959).
93. K. A. Andrianov, Zhur. Obshch. Khim., 16, 633 (1946).
94. K. A. Andrianov and L. M. Volkova, Zhur. Obshch. Khim., 30, 2393 (1960).
95. P. K. Dutt, Sci. and Culture (Calcutta), 22, 109 (1956); Chem. Abs., 53, 6995 (1959).
96. M. J. Hunter, US P. 2 645 624 (1953); Chem. Abs., 47, 10 274 (1953).
97. R. O. Sauer, J. Amer. Chem. Soc., 68, 138 (1946).
98. L. Lasocki, Roczniki Chem., 31, 305, 837 (1957); Chem. Abs., 51, 16 282 (1957); 52, 1005 (1958).
99. H. J. Fletcher and M. J. Hunter, B. P. 618 459 (1949); Chem. Abs., 43, 6221 (1949).
100. H. J. Hunter, H. J. Fletcher, and C. C. Currie, US P. 2 415 389 (1947); Chem. Abs., 41, 3116 (1947).
101. H. J. Fletcher and M. J. Hunter, J. Amer. Chem. Soc., 71, 2918 (1949).
102. K. A. Andrianov and Shu-Mêng Sun, Vysokomol. Soed., 2, 552 (1960).
103. R. Okawara, T. Ando, and K. Ayama, Technol. Repts. Osaka Univ., 8, 171 (1958); Chem. Abs., 53, 12 160 (1959).
104. R. Okawara, Technol. Repts. Osaka Univ., 7, 447 (1957); C., 131, 4855 (1960).
105. M. Momonoi, N. Suzuki, O. Yamaguchi, Nippon Kagaku Zasshi, J. Chem. Soc. Japan, 78, 1600 (1957); Chem. Abs., 54, 1376 (1960).
106. M. F. Shostakovskii and Kh. I. Kondrat'ev, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1041 (1959).
107. T. Tanaka and R. Okawara, Bull. Chem. Soc. Japan, 28, 364 (1955).
108. R. Okawara, Kogyo Kagaku Zasshi, J. Chem. Soc. Japan, Ind. Chem. Sect., 61, 690 (1958); Chem. Abs., 55, 11 287 (1961).
109. R. Okawara and S. Imaeda, Bull. Chem. Soc. Japan, 31, 194 (1958), Chem. Abs., 52, 15 422 (1958).
110. General Electric Co., B. P. 993 881 (1961); Brit. Pat. Abstr., 5, 26 (1965).
111. K. A. Andrianov, T. N. Ganina, N. N. Sokolov, and E. N. Khrustaleva, Zhur. Obshch. Khim., 30, 2777 (1960).
112. I. A. Shikhiev, G. F. Askerov, and Sh. V. Garaeva, Zhur. Obshch. Khim., 38, 639 (1968).
113. G. H. Wagner and C. E. Erickson, US P. 2 731 485 (1956); Chem. Abs., 50, 8247 (1956).
114. S. I. Sadykh-Zade and A. D. Petrov, Zhur. Obshch. Khim., 29, 3194 (1959).
115. S. I. Sadykh-Zade and A. D. Petrov, "Khimiya i Prakticheskoe Primenenie Kremneorganicheskikh Soedinenii" (The Chemistry and Practical Applications of Organosilicon Compounds), Leningrad, 1958, Vol. 1, p. 212.
116. K. A. Andrianov, L. M. Volkova, and V. N. Talanov, Izv. Akad. Nauk SSSR, Ser. Khim., 2045 (1963).
117. C. R. Krüger and E. G. Rochow, Angew. Chem., 74, 491 (1962).
118. C. R. Krüger and E. G. Rochow, Inorg. Chem., 2, 1295 (1963).
119. K. A. Andrianov, V. N. Talanov, L. M. Khananashvili, T. V. Minakova, and N. P. Gashnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 661 (1968).
120. K. A. Andrianov, T. V. Vasil'eva, and I-Ming Li, Izv. Akad. Nauk SSSR, Ser. Khim., 1847 (1963).
121. K. A. Andrianov, V. N. Talanov, L. M. Khananashvili, and E. S. Sobolev, Izv. Akad. Nauk SSSR, Neorg. Materialy, 1849 (1965).
122. K. A. Andrianov, V. N. Talanov, L. M. Khananashvili, Yudit Gelei, and N. P. Gashnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 2546 (1967).
123. T. A. Robinson, BRD P. 1 252 682 (1964); B. P. 1 061 225 (1965); Dutch P. 6 510 605 (1964); Chem. Abs., 65, 10 622 (1966).
124. M. G. Voronkov and L. Zagata, Zhur. Obshch. Khim., 38, 2327 (1968); Izv. Akad. Nauk Latv. SSR, Ser. Khim., 507 (1964).
125. L. Zagata, Candidates Thesis, Division of Chemical and Biological Sciences, Academy of Sciences of the Latvian SSR, Riga, 1969.
126. S. B. Dolgoplosk, T. V. Kurlova, E. G. Kagan, V. P. Mileshkevich, A. L. Klebanskii, S. N. Borisov, L. D. Akhanova, and E. Sh. Paper, USSR P. 236 472 (1967); Byull. Izobret., No. 7, 20 (1969).
127. R. M. Pike, US P. 3 046 294 (1959); B. P. 969 213 (1959); Chem. Abs., 57, 15 153 (1962).
128. L. H. Sommer and E. L. Warrick, B. P. 671 579 (1952); US P. 2 607 792 (1952); Chem. Abs., 47, 3869, 9346 (1953).
129. P. L. Brown and J. F. Hyde, US P. 3 146 251 (1961); French P. 1 327 545 (1963); Chem. Abs., 60, 553 (1964).
130. G. M. Omietanski, French P. 1 399 256 (1963); US P. 3 309 390 (1963); BRD P. 1 219 934 (1963); Chem. Abs., 63, 16 383 (1965).
131. G. M. Omietanski, BRD P. 1 219 934 (1963); Auszüge aus den Pat., 12, No. 26, 12 (1966).
132. M. Schatz, Czech. P. 116 688 (1964); Chem. Abs., 65, 17 179 (1966).
133. R. J. Boot and A. Torkelson, US P. 3 132 167 (1960); Chem. Abs., 61, 3233 (1964).
134. G. R. Lucas and R. W. Martin, J. Amer. Chem. Soc., 74, 5225 (1952).
135. G. R. Lucas and R. W. Martin, US P. 2 600 307

(1950); French P. 1 041 648 (1950); C., 126, 215 (1955).
136. S. Fukukawa and S. Kohoma, Science Ind. (Japan), 28, 261 (1954); Chem. Abs., 50, 791 (1956).
137. E.D. Brown, Belgian P. 658 944 (1964); Chem. Abs., 64, 11 249 (1966).
138. G. I. Harris, J. Chem. Soc., 5978 (1963).
139. F. S. Kipping, J. Chem. Soc., 101, 2125 (1912).
140. P. I. Prescott and T. G. Selin, French P. 1 374 620 (1962); Chem. Abs., 62, 7797 (1965).
141. R. N. Lewes, J. Amer. Chem. Soc., 70, 1115 (1948).
142. M. S. Shostakovskii, D. A. Kochkin, Kh. I. Kondrat'ev, and V. M. Rogoz, Zhur. Obshch. Khim., 26, 3344 (1956).
143. H. A. Vaughn, US P. 3 328 323 (1963); B. P. 1 039 445 (1966); Chem. Abs., 65, 20 336 (1966).
144. G. Schott and H. Berge, Z. anorg. Chem., 297, 44 (1958).
145. R. Robinson and F. S. Kipping, J. Chem. Soc., 101, 2156 (1912).
146. R. Robinson and F. S. Kipping, J. Chem. Soc., 101, 2142 (1912).
147. K. A. Andrianov and B. A. Izmailov, Izv. Akad. Nauk SSSR, Ser. Khim., 1070 (1967).
148. K. C. Frisch, P. A. Goodwin, and R. F. Scott, J. Amer. Chem. Soc., 74, 4584 (1952).
149. K. C. Frisch and P. A. Goodwin, US P. 2 678 938 (1952); Off. Gaz., 682, 725 (1954).
150. K. C. Frisch and R. B. Young, J. Amer. Chem. Soc., 74, 4853 (1952).
151. K. C. Frisch and R. B. Young, US P. 2 671 101 (1954); Chem. Abs., 49, 2499 (1955).
152. M. Momonoi, N. Suzuki, and Nippon Kagaku Zasshi, J. Chem. Soc. Japan, 78, 581 (1957); Chem. Abs., 53, 5169 (1959).
153. K. A. Andrianov and A. A. Zhdanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1076 (1958).
154. A. A. Zhdanov and K. A. Andrianov, "Khimiya i Prakticheskoe Primenenie Kremneorganicheskikh Soedinenii" (The Chemistry and Practical Applications of Organosilicon Compounds), Leningrad, 1958, Vol. 2, p. 100.
155. K. A. Andrianov and A. A. Zhdanov, J. Prakt. Chem., 9, 75 (1959).
156. Shang-An Lin, Sun Yat-Sun Univ. J. Nat. Sci., No. 3, 9 (1959); Chem. Abs., 56, 10178 (1962).
157. S. W. Kantor, J. Amer. Chem. Soc., 75, 2712 (1953).
158. A. L. Klebanskii, E. G. Kagan, Yu. A. Yuzhelevskii, A. V. Kharlamova, and E. P. Sergeeva, USSR P. 221 293 (1967); Byull. Izobret., No. 6, 184 (1969).
159. L. S. Moody, US P. 2 567 742 (1951); Chem. Abs., 47, 145 (1953).
160. J. F. Hyde, J. Amer. Chem. Soc., 75, 2166 (1953).
161. F. S. Kipping and R. Robinson, J. Chem. Soc., 105, 484 (1914).
162. Z. N. Nudel'man, K. A. Andrianov, and G. B. Kudryavitskaya, Vysokomol. Soed., 4, 440 (1962).
163. Shang-An Lin and J. Lin, Scientia (Peking), 625 (1957); Chem. Abs., 53, 10 016 (1959).
164. N. E. Daughenbaugh, US P. 3 179 678 (1962); Belgian P. 630 247 (1962); Chem. Abs., 61, 687 (1964).
165. G. H. Barnes and N. E. Daughenbaugh, J. Org. Chem., 31, 885 (1966).
166. A. S. Hay, US P. 3 099 640 (1961); B. P. 984 151 (1961); Chem. Abs., 60, 552 (1964).
167. N. N. Sokolov, Zhur. Obshch. Khim., 29, 259 (1959).
168. K. A. Andrianov, V. V. Astakhin, and V. K. Pyzhov, Izv. Akad. Nauk SSSR, Otd. Khim., Nauk, 2242 (1962).
169. K. A. Andrianov and M. A. Sipyagina, Izv. Akad. Nauk SSSR, Otd. Khim., Nauk, 1392 (1962).
170. K. A. Andrianov, N. A. Kurasheva, I. K. Kuznetsova, and E. N. Gerkhardt, Dokl. Akad. Nauk SSSR, 140, 365 (1961).
171. M. M. George, W. Holbrook, and P. L. Brown, US P. 2 915 544 (1958); B. P. 859 285 (1958); French P. 1 207 279 (1958); Chem. Abs., 54, 7561 (1960).
172. S. Chrzczonowicz and Z. Lasocki, Roczniki Chem., 35, 127 (1961).
173. M. G. Voronkov, N. G. Sviridova, and S. N. Borisov, Zhur. Obshch. Khim., 39, 1999 (1969).
174. M. G. Voronkov, N. G. Sviridova, and S. N. Borisov, USSR P. 263 595 (1968); Byul. Izobret., No. 8, 21 (1970).
175. A. I. Petrashko, Dokl. Akad. Nauk SSSR, 180, 1116 (1968).
176. K. A. Andrianov and V. V. Severnyi, Zhur. Obshch. Khim., 32, 1633 (1961).
177. K. A. Andrianov and A. I. Petrashko, Vysokomol. Soed., 1, 1516 (1959).
178. K. A. Andrianov and A. A. Zhdanov, Dokl. Akad. Nauk SSSR, 114, 1005 (1957).
179. M. V. Sobolevskii, L. A. Chistyakova, D. V. Nazarova, and V. V. Kirillina, Plast. Massy, No. 10, 17 (1962).
180. K. A. Andrianov, M. A. Sipyagina, N. P. Gashnikova, and Z. M. Frolova, Izv. Akad. Nauk SSSR, Neorg. Materialy, 1, 1441 (1965).
181. K. A. Andrianov and M. A. Sipyagina, Izv. Akad. Nauk SSSR, Neorg. Materialy, 4, 2016 (1968).
182. J. F. Hyde, US P. 2 567 110 (1951); Chem. Abs., 45, 10 676 (1951).
183. A. L. Suvorov and S. S. Spasskii, Trudy, Inst. Khim. Ural'sk. Fil. Akad. Nauk SSSR, No. 13, 25 (1966).
184. M. V. Sobolevskii, L. A. Chistyakova, D. V. Nazarova, and V. V. Kirillina, USSR P. 141 156 (1961); Byull. Izobret., No. 1, 18 (1961).
185. C. Schneider and G. Berg, Makromol. Chem., 54, 171 (1962).
186. A. N. Lazarev, T. F. Tenisheva, and V. P. Davydova, Dokl. Akad. Nauk SSSR, 158, 648 (1964).
187. K. A. Andrianov, Uspekhi Khim., 26, 895 (1957).

Institute of Organic Synthesis,
Academy of Sciences of the
Latvian SSR, Riga

Lebedev All-Union Institute
of Synthetic Rubber, Leningrad