

**REVIEW****Polyfunctional Si-N Containing Modifiers of Industrial Polymers: Synthesis, Properties and Use**

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Polyfunctional silicon-organic oligomers containing Si-N, Si-O groups, as well as arylene and heteroarylene fragments in the main chains of macromolecules are reviewed. The methods of their synthesis and mechanisms of the formation are discussed. The properties and spheres of their application are considered.

**Key Words:** Silazane, Heterocycle, Polymer, Thermal stable, Properties, Industrial polymers, Modification, Use.

**INTRODUCTION**

Silazaneorganic oligomers and polymers are one of the applicable siliconorganic polyfunctional compounds with inorganic-organic main chains<sup>1-20</sup>. They are used for production of various important technical compositions and materials with specific properties such as polymer varnishes and coatings, water-repellents, polymer ceramics and silicon-nitride fibers, *etc.* They are also successfully used in nanotechnology and as modifiers of the other organic and elementorganic oligomers, polymers and materials on their basis. Among them, by thermal, adhesive, thermomechanical and radiation-stable properties distinguish oligomers and polymers containing arylene and heteroarylene fragments in the macrochains<sup>15-20</sup>.

The literature described practically important and technologically justified four methods for obtaining polyfunctional siliconorganic polymers with organic-inorganic main chains containing Si-N and Si-O groups simultaneously. (a) The polymerization polycondensation method of heterocycles containing silicon-nitrogen heterocycles-organocyclosilazane and organocyclosiloxanes with arylene and heteroarylene bisphenols; (b) The catalytic polymerization condensation of organosiloxane heterocycles with various difunctional organosilicon and other compounds containing hydroxy groups; (c) The co-oligomerization of siliconorganic heterocycles with siliconorganic difunctional compounds; (d)  $\alpha,\omega$ -dihydridoorganoorganosiloxanes polycombination with polyfunctional divinyl and diallyl compounds.

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The priority of the first method is stipulated according to the following features<sup>22</sup>, mainly: (a) The ability of carrying out the reaction without catalysts; (b) The possibility of removing completely of side-product without any additional special experimental procedures; (c) The relatively high yield of the obtaining polymers; (d) The experimental simplicity of the procedure; (e) The easiness of providing the control of the reaction; (f) The ability to vary the properties of the obtaining polymers; (g) The relative availability of the initial silazane monomers the preparation of which is easy; (h) The ability of modifying the properties of various commercial organic and elementorganic materials through application a small amount of the obtained polymers.

The second method according to the technological simplicity is similar to the first one. In this method production of side-products is excluded. The priority of the third method is the simplicity and availability.

The fourth method allows to synthesize the polyfunctional siliconorganic polymers with linear macrochains with the regular structure containing simultaneously Si-N-, Si-O- and N-H-groups at low temperature with applicable perspective in modern techniques<sup>21-55</sup>.

In practice the above mentioned methods are applied for obtaining of the siliconorganic heterochain polymers with specific properties and are considered as a non-traditional method for their synthesis<sup>21,22</sup>.

The present authors have analyzed the scientific works of well-known authors of these fields and original experimental results. In present review article it is shown that the described methods are experimentally simple and available, thus allowing to obtain different type silicon-organic polymers<sup>22-33</sup>.

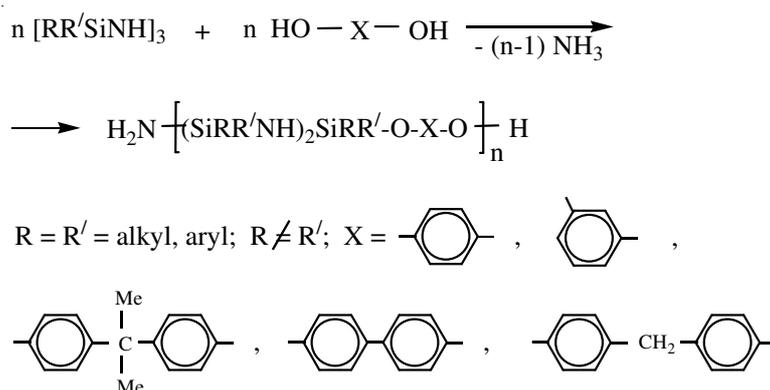
In the review, according to the modern achievements are discussed the kinetics and mechanisms of hydride polyaddition and polymerization polycondensation reactions. Based on this simultaneously Si-N- and Si-O- groups obtained through the hydride polyaddition and polymerization polycondensation reactions, for production of new nonmetal materials, mainly, high stable polymeric composites, antibiocorrosion protective and covers, nanohybrid materials for organic-inorganic support production and for features modification of poly-functional synthetic industrial materials.

This will encourage the development of chemistry and physics of nontraditional synthetic materials explained the influence of structure and reaction-ability of initial monomers on the direction of reaction, on the structure of polymers and feature.

### **1. Polymerization-polycondensation of silicon-nitrogen containing heterocycles with various aromatic and siliconorganic diols**

The first efforts aimed for obtaining polymers with inorganic and organic-inorganic macromolecular chains using combined polymerization and condensation processes were published in the 60s. Elliot and Breed used aromatic diols instead of diamines in a reaction with organocyclo-silazanes to achieve polymerization-

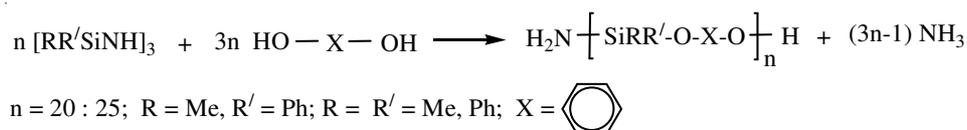
condensation. It appeared that with an equimolar ratio of the initial reagents the reaction was conducted quite intensively both in bulk and in solvent (toluene, benzene and xylene) releasing ammonia and forming high-molecular compounds with Si-N links in a chain<sup>29</sup>:



**Scheme-1.1**

Boiling of synthesized organosilazaoxyarylene polymers with ethyl alcohol for 1 h does not lead to any noticeable reduction of viscosity and their destruction starts only at 350-400 °C.

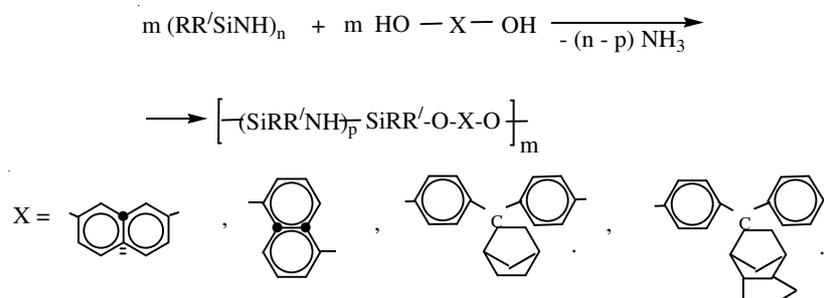
An increase of the molar fraction of the original aromatic diol to 1:3 induces complete replacement of the NH-groups in a polymer chain with residues of the aromatic diol, thereby producing relatively low-molecular products of the siloxyarylene structure:



**Scheme-1.2**

Nevertheless, even the products formed in this case possess considerably high thermooxidizing stability.

An investigation of reaction of organic diols of different structures with organocyclosilazanes of different cycle sizes and different nature of organic radicals at silicon atoms was aimed at clearing up the effect of diol and organocyclosilazane structures upon the polymerization-condensation process (Table-1.1). The reaction of dialkyl-, methylphenyl- and diphenylcyclosilazanes with dioxynaphthalenes and polycyclic bisphenols proceeded in bulk until the ammonia isolation stops. With an equimolar ratio of the reagents the reaction proceeds as follows<sup>2,3</sup>:

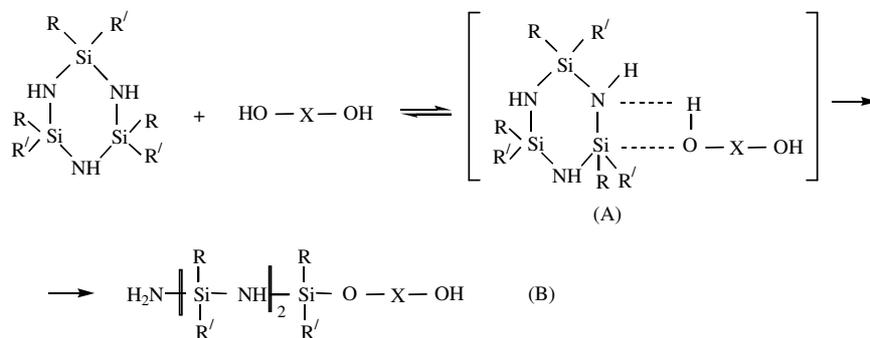


Scheme-1.3

The reaction rate, the viscosity and yield of the polymers formed depend considerably on the diol and organocyclosilazane structures (Table-2.1), while the completeness of the reaction on the reagents ratio.

In all the cases in the initial stage of the reaction the kinetic curves of ammonia isolation (Figs. 1.1 and 1.2) reveal an induction period, its length growing with the radical volume on the silicon atom.

At the initial stage of the reaction the induction period seems to depend on the establishment of a stationary concentration of the transition complex A, which then decays in the following way:



where X - the residue of the aromatic diols

Scheme-1.4

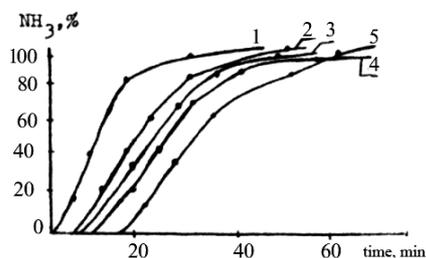
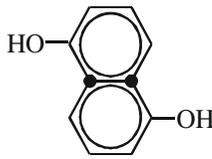
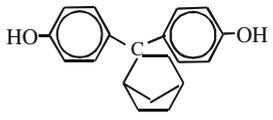


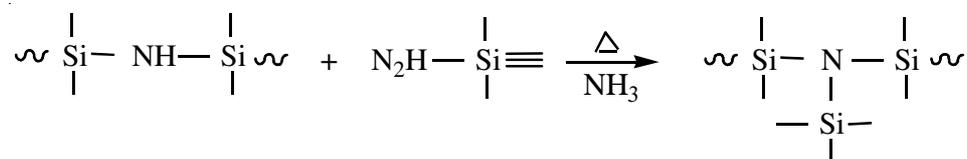
Fig. 1.1. Dependence of amount of separated ammonia on time in the reaction of 1,5-dihydroxynaphthalene with  $[\text{RR}'\text{SiNH}]_3$  (1M:1M) (Table-1.1): (1).  $\text{R} = \text{R}' = \text{Me}$ ; (2).  $\text{R} = \text{Me}$ ;  $\text{R}' = n\text{-Bu}$ ; (3).  $\text{R} = \text{R}' = \text{Et}$ ; (4).  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$ ; (5).  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{C}_8\text{H}_{17}$

TABLE-1.1  
 POLYSILAZASILOXIARILENS BASED ON POLYCYCLIC BISPHENOLS AND AROMATIC DIOLS

	[RR'SiNH] <sub>3</sub>		Diols	React. temp. (°C)	React. time (h)	Separated ammonia (%)	Formula of the elementary rings of polymers	Yield of polymers (%)	η <sub>sp</sub> (1 % solution in toluene)	T <sub>gam.</sub> (°C)
	R	R'								
1	Me	Me		130	0.52	101	$\left[ (\text{SiMe}_2\text{-NH})_2\text{-SiMe}_2\text{-O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \text{-O} \right]_n$	89.0	1.29	8
2	Me*	Me*		130	0.60	100		73.0	0.75	–
3	Me	Ph		140	1.00	106	$\left[ \text{SiRR}'\text{-NH-SiRR}'\text{-O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \text{-O} \right]_n$	–	0.82	27
4	Ph	Ph		170-180	2.00	84		–	0.32	–
5	Me	Me		130	0.5	100	$\left[ (\text{SiMe}_2\text{-NH})_2\text{-SiMe}_2\text{-O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \text{-O} \right]_n$	90.0	1.01	-10
6	Me*	Me*		130	0.6	91		74.0	0.69	–
7	Me	Ph		140	1.2	97		83.0	0.50	30
8	Ph	Ph		160-170	2.2	81	$\left[ \text{SiRR}'\text{-NH-SiRR}'\text{-O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \text{-O} \right]_n$	–	0.23	–
9	Me	<i>n</i> -Bu		180	0.5	101		89.0	0.58	-13
10	Et	Et		180	0.8	101	$\left[ (\text{SiMe}_2\text{-NH})_2\text{-SiMe}_2\text{-O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \text{-O} \right]_n$	81.0	0.60	-25
11	Me	<i>n</i> -C <sub>8</sub> H <sub>17</sub>		180	1.0	100		91.0	0.45	-42
12	Me	Me		130	1.5	100		96.0	0.81	36
13	Me	Me		140-150	1.2	97	$\left[ \text{SiRR}'\text{-NH-SiRR}'\text{-O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \text{-O} \right]_n$	95.0	0.80	–
14	Me	Ph		130-150	2.0	98		96.5	0.40	56
15	Ph	Ph		170-180	3.0	94		–	0.34	63

The resultant compound **I** attack the new molecule of the cycle, forming a similar complex which then either undergoes decay or starts a condensation reaction with the new diol molecule. Consequently, the growth of a polymer chain is due both to the polymerization reaction of cyclic silazane proceeding with its opening and to condensation of the end amine and hydroxyl groups. The hydroxyl group can attack not only cyclic compounds, but also linear sections of a silazane-group containing chain, thus leading to the statistical distribution of structural units in a macromolecular chain.

As it is evident from Table-1.1, conversion over ammonia, in some cases, exceeds the one calculated from the quantity of the original diol. When conversion over ammonia was less than one mole on mole of the initial diol, the reaction had been continuing up to 1.03-1.05 moles of  $\text{NH}_3$  on one mole of the diol. The polymers transformed into insoluble, infusible state. These facts demonstrated, that not only the reaction of chain increase occurs, but also the reaction of *trans*-amination takes place due to the interaction of NH-groups, being formed during the process of chain increase, with  $=\text{Si-NH-Si}=\text{}$  groups presenting into the system. It causes formation of branching and retina macromolecules with trisilylamine groups at the knots of branching:

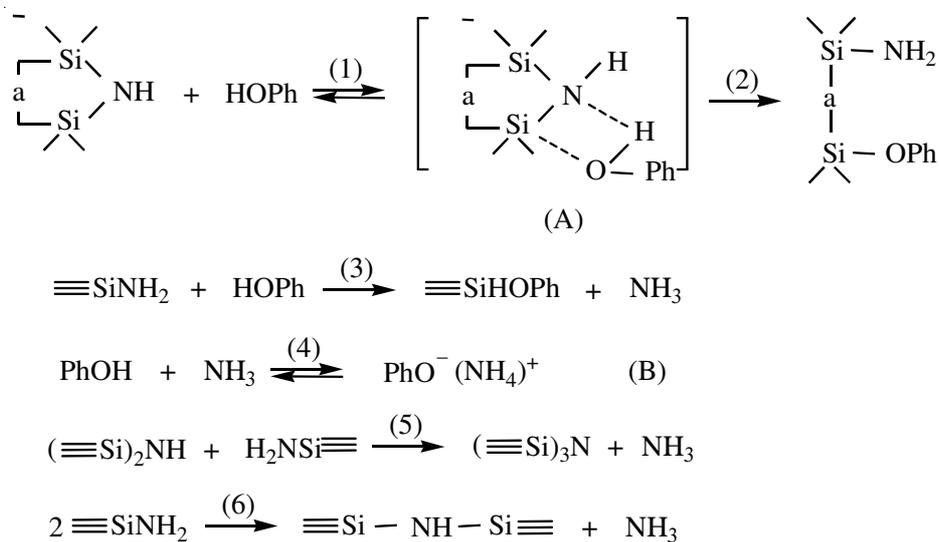


**Scheme-1.5**

The model reactions of some of Si-N containing heterocycles with phenol (at the ratio 1:2) were studied and the kinetic curves of isolation of ammonia were obtained for investigating the principal CPC process. Considering the above mentioned experimental data the mechanism of the reaction was described by system of differential equations. Several versions of the mechanisms, were calculated with the aim of choosing the most probable one. The simplest mechanism comprising the stage of the opening of cycles over Si-N bond and of further heterofunctional condensation of the formed  $\text{NH}_2$ -groups with hydroxy groups did not lead to any satisfactory approximation for solving the extreme problem.

At the given precision of the experiment the most satisfactory result from the point of view of minimization of average deviation (Fig. 1.2) is the following mechanism:

The velocity constants of the elementary stages were determined (Table-1.2) by minimizing the average deviation of the points of the experimental curve from the theoretical function for separation of ammonia.

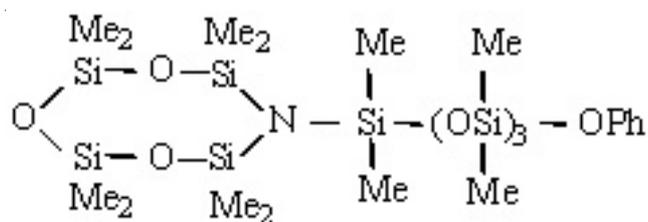


Scheme-1.6

 TABLE-1.2  
 RATE CONSTANTS OF MODEL REACTION OF THE COMBINED  
 POLYMERIZATION-CONDENSATION PROCESS

Si-N-containing heterocycles	$k_{1,2}$	$k_3$	$k_5$	$k_6$
$  \begin{array}{c} \text{Me}_2 \\   \\ \text{Me}_2\text{SiOSiSiMe}_2 \\   \\ \text{NH} \end{array}  $	1.20	20.3	0.68	0.94
$  \begin{array}{c} \text{Me}_2\text{Si} - (\text{CH}_2)_3 - \text{SiMe}_2 \\   \\ \text{NH} \end{array}  $	0.20	10.12	1.04	0.94
$  \begin{array}{c} \text{Me}_2\text{Me}_2 \\   \\ \text{Me}_2\text{SiOSiSiOSiSiMe}_2 \\   \\ \text{NH} \end{array}  $	0.05	13.19	1.10	0.90

The formation of transition complex has been established by  $^1\text{H}$  NMR method. The process of transamination (stage 5) was established using  $^1\text{H}$  NMR-, UV-spectra and chromatography analysis. The compound of the following structure was shown to form:



Scheme-1.7

The kinetic data reveal (Table-1.2) that the limiting stage is the formation of a transition complex (A) and the reaction of the cyclic silazane opening giving rise to the induction period of the reaction. However, the observed induction period (Fig. 1.1) can be seemingly due to ammonia binding (reaction 4). Besides, the resultant nucleophilic particles (B) may act as an effective catalyst in the condensation reactions. When diols are used reactions (2) and (3) are definitive at the chain growth stage. A simultaneous side reaction (5) is possible, also catalyzed by nucleophilic molecules (B), thus leading to macromolecular chain branching and eventually to polymer structure formation. Indeed, when a polymer mass is subjected to prolonged heating up to 180-200 °C, the polymers change to a non-melting and insoluble state.

Most of the resultant polymers are hard rubber-like substances and their elastic properties depend on the size of the siliconorganic fragment in the elementary link of a macromolecular chain and the nature of the organic radicals on the silicon atom. Polymers of the highest viscosity ( $[\eta] = 0.75-0.87$  dl/g) and satisfactory elastic properties were obtained on the basis of hexamethylcyclotrisiloxane and dioxynaphthalene with 1:1 ratio.

Methylphenyl- and diphenylcyclotrisilazanes form polymers with higher temperatures of vitrification (Table-1.1). In case of organocyclotrisilazanes with large aliphatic radicals at silicon atoms highly viscous liquids are formed.

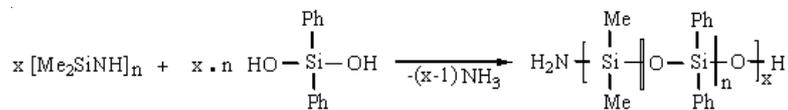
It is noteworthy that the importance of the exchange reactions in the process of polymerization-condensation increases with the growth of the diol molar fragment in the original mixture. With a three-fold excess of diol the reaction produces fragile vitreous materials. In such a case<sup>10</sup>, the products form contain an elementary link solids which does not contain silazane groups and which have a high molecular weight and  $\eta_{sp} = 0.09-0.13$ .

Polymers based on diorganocyclotrisilazane and aromatic diols are readily soluble in benzene, toluene, chloroform, but insoluble in saturated hydrocarbons.

The character of polymer thermomechanical curves depends on the ratio of the original compounds, the volume of radicals at silicon atoms and the nature of the aromatic diol. When the permanently applied load is increased (from 30 to 100' the highly elastic area vanishes and  $T_{vit}$  of the polymers drops significantly; meanwhile, with  $[-SiRR'-O-X-O-]_n$ -type polymers, *i.e.*, polymers without any silazane groups in chains, there is no elastic area on the curves and the polymers demonstrate comparatively high temperatures of vitrification ( $T_{vit} = 38-93$  °C).

According to the thermogravimetric data, mass losses, as low as 2-5 % was observed in polymers obtained from hexamethylcyclotrisiloxane and aromatic diol at an equimolar ratio at 400 °C.

A polymerization-polycondensation process can be carried using organic diamines and diols. Thus, a reaction of diorganocyclotrisilazanes with a three-four-fold molar excess of dihydroxydiphenylsilane yielded polyorganosiloxanes with a high content of diphenylsiloxy links in the polymer chains<sup>22,33</sup>:



where  $n = 3$  or  $4$ .

**Scheme-1.8**

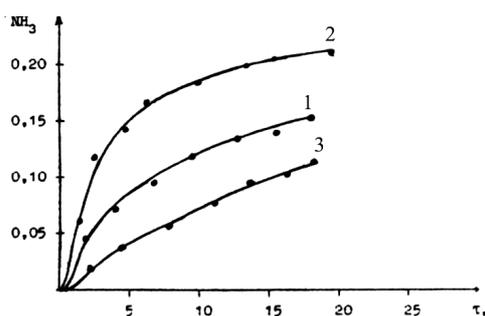


Fig. 1.2. Kinetical curves for the systems phenol:Si-N containing cycles: (1)  $[\text{Me}_2\text{Si}-(\text{CH}_2)_3-\text{SiMe}_2]$ ; (2)  $[\text{Me}_2\text{SiO}]_2(\text{Me}_2\text{Si}_2\text{NH})$ ; (3)  $[\{\text{Me}_2\text{SiO}\}_3(\text{Me}_2\text{SiNH})]$

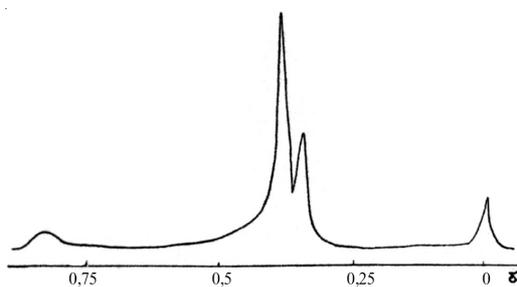


Fig. 1.3.  $^1\text{H}$  NMR spectrum of the *trans*-isomer of  $[\text{MePhSiNH}]_3$

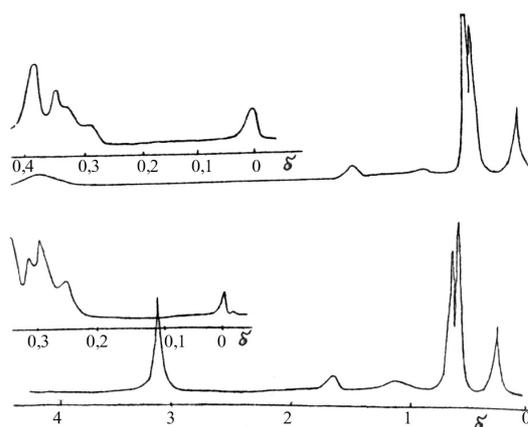


Fig. 1.4.  $^1\text{H}$  NMR spectrum of the mixture of the *trans*-isomer of  $[\text{MePhSiNH}]_3$  and phenol after mixing of the initial compounds at 4th min (a) and 45th min (b)

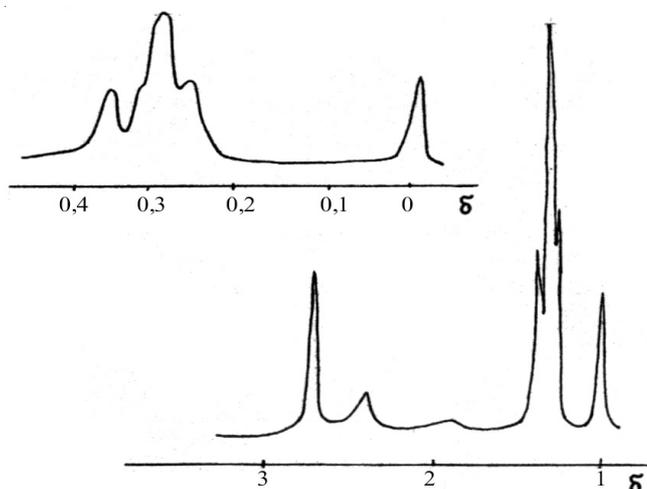


Fig. 1.5.  $^1\text{H}$  NMR spectrum of the mixture of the *trans*-isomer of  $[\text{MePhSiNH}]_3$  and phenol after mixing of the initial compounds at 429 min

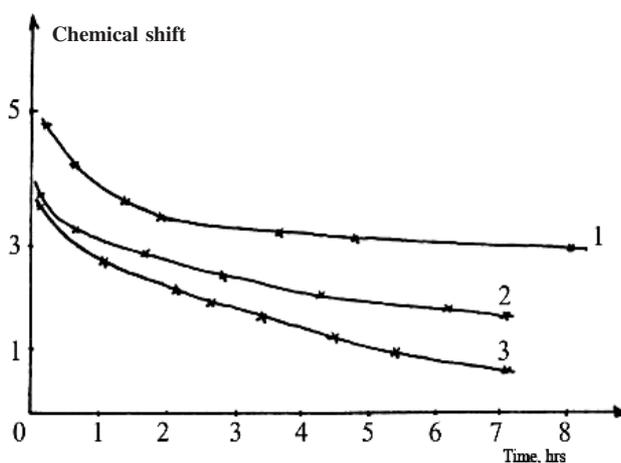
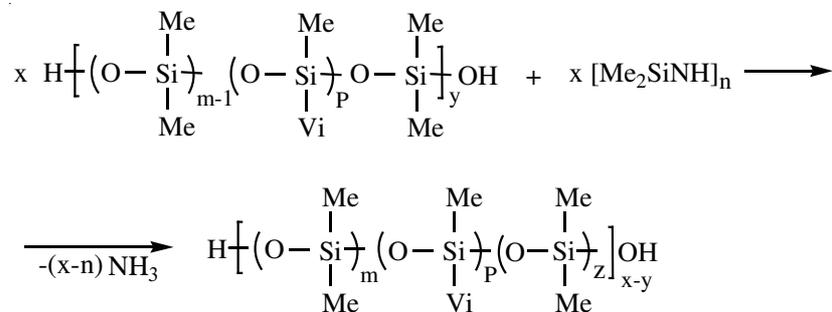


Fig. 1.6. Dependence of chemical shifts of hydroxy groups protons on time in mixture of the phenol and *trans*-isomer of  $[\text{MePhSiNH}]_3$  at different molar ratio: 1. 0.5:1; 2. 0.65:1; 3. 1:0.5

The polymers obtained are of interest as bonds to be used in the formation of composite materials with high thermal and irradiation stability.

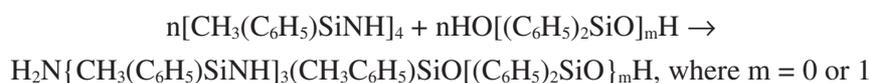
Interesting results have been obtained in a recent study of a reaction between  $\alpha,\omega$ -dihydroxypolydimethyl(methylvinyl)siloxanes and dimethylcyclosilazanes. The reaction also proceeded easily, in mass, with isolation of gas ammonia, according to the polymerization-polycondensation mechanism with ammonia isolation:

**Scheme-1.9**

Therefore, the molecular mass of polymethyl(methylvinyl)siloxanes increases forming high-molecular elastomers ( $[\eta] = 1.4\text{-}1.8$  dl/g). The optimal conditions of the process require a reaction temperature  $175$  °C and diol-to-hexamethylcyclotrisilazane ratio 1:2. the lower the temperature, the slower the reaction rate. Meanwhile, at higher temperatures the polymer formed has an insufficient MM because hexamethylcyclotrisiloxane boils out before it has time to complete the reaction with diol (the trimer  $T_{b.p.}$  is  $180$  °C); the duration of this process is directly related to the original  $\alpha,\omega$ -dihydropolydimethyl(methylvinyl)siloxanes MM. The characteristic viscosity in toluene observed in the diol condensation product at MM = 6000 was 0.5 dl/g after 10 h, while at MM = 30,000 it was 1.6 dl/g after the same period of treatment.

The physical and chemical characteristics of rubber obtained from synthesized polymers and subject to thermal ageing are superior to those of rubber obtained from industrial rubber polydimethyl(siloxane, since the rubber obtained by polymerization polycondensation of dihydroxypolydimethyl(methylvinyl)siloxanes with dimethylcyclotrisilazanes without acid or alkaline catalysts, is naturally free of the latter which usually deteriorate the thermal stability of rubber.

The reactions of tetramethyltetraphenethylcyclotetrasilazane with dihydroxydiphenylsilane and 1,3-dihydroxytetraphenylsiloxane were studied at the molar ratio 1:1. The processes proceed *via* a polymerization mechanism releasing ammonia and forming a corresponding polyorganosilazaoxanes by the following **Scheme**<sup>33</sup>:

**Scheme-1.10**

The reaction does not proceed even at  $130\text{-}140$  °C, when it is carried out in an aromatic solvent (toluene, ditolylmethane) due to high hydrolytic stability of cyclosilazane with phenethyl radical attached to the silicon atom, while in bulk the reaction begins at  $70$  °C achieving the maximum of conversion in terms of isolating

ammonia (80-98 %) in the range of 110-120 °C. At temperatures higher than this, the conversion of ammonia reduces. Especially it is noticeable in the case of the nitrogen content in the polymer, after it is placed under reduced pressure due to replacing of silazanic bonds by siloxanic ones.

Investigation of the kinetics of the reaction monitors the process to be characterized by the induction period achieving 0.5 h in case of the reaction with dihydroxydiphenylsilane at 98 °C, while increasing the temperature more than 130 °C, it diminishes within 3 min.  $M_n$  of the polymers is of the order of  $6.0-6.7 \times 10^4$ . Gel chromatographic analysis demonstrates sufficiently narrow distribution of MM in the polymers.

TABLE-1.3  
CONDITIONS OF THE POLYMERIZATION CONDENSATION OF  
ORGANOCYCLOSILAZANS WITH  $\alpha,\omega$ -DIHYDROXPOLYORGANOSILOXANES

Initial monomers Cyclosilazane {Dio}	React. temp. (°C)	React. time, h (Amount of separated NH <sub>3</sub> , %)	$\eta_{sp}$ (T <sub>g</sub> , °C)	Elemental analysis (%): Found (calcd.)			
				C	H	N	Si
[(Me <sub>2</sub> SiNH) <sub>2</sub> (Me <sub>2</sub> SiO) <sub>2</sub> ] {HO[Me <sub>2</sub> SiO] <sub>3</sub> H}	80	2.80 (86.00)	0.25 (-)	32.59 (32.46)	8.35 (8.36)	- (2.70)	37.74 (37.95)
[(Me <sub>2</sub> SiNH) <sub>2</sub> (Me <sub>2</sub> SiO) <sub>2</sub> ] {HO[Me <sub>2</sub> SiO] <sub>10</sub> H}	150-160	3.20 (72.00)	0.33 (-100)	- (-)	- (-)	- (-)	- (-)
[(Me <sub>2</sub> SiNH) <sub>2</sub> (Me <sub>2</sub> SiO) <sub>2</sub> ] {HO[Me <sub>2</sub> SiO] <sub>15</sub> H}	150-160	4.70 (91.00)	0.50 (-)	38.60 (32.49)	8.20 (8.13)	1.21 (0.99)	37.74 (37.86)
[(Me <sub>2</sub> SiNH) <sub>2</sub> (Me <sub>2</sub> SiO) <sub>2</sub> ] {HO[Me <sub>2</sub> SiO] <sub>55</sub> H}	180-190	10.00 (87.00)	0.68 (-)	39.92 (40.48)	7.94 (8.16)	- (0.32)	37.43 (37.91)
[Me(Et)SiNH] <sub>3</sub> {HO[Me <sub>2</sub> SiO] <sub>15</sub> H}	150-160	2.50 (89.50)	0.27 (+68)	- (-)	- (-)	- (-)	- (-)
[C <sub>6</sub> H <sub>13</sub> Si(NH) <sub>1.5</sub> ] <sub>6</sub> {[PhSiO(OH)] <sub>4</sub> }	101*	14.15 (93.70)	0.10 (+90)	54.32 (55.33)	7.94 (8.14)	6.36 (7.53)	20.83 (21.58)
[C <sub>6</sub> H <sub>13</sub> Si(NH) <sub>1.5</sub> ] <sub>6</sub> {[PhSiO(OH)] <sub>4</sub> }	150-200	14.00 (78.00)	0.13 (-100)	54.44 (55.33)	7.98 (8.14)	7.08 (17.53)	21.20 (21.58)

The combined polymerization-condensation reaction of *tris*(tricyclodecylmethyl)cyclotrisilazane with the oligodimethylsiloxanes ( $m = 12, 35$  and  $72$ ) at molar ratio 1:1<sup>34-36</sup> was also investigated. It was established that conditions of the reaction, T<sub>g</sub>, yield and specific viscosity of the polymers, depend on the length of siloxane chain of  $\alpha,\omega$ -dihydroxythetmethylsiloxane (Table-1.4)<sup>21</sup>. As it is evident from Table-1.4, increasing the extent of polymerization of the oligomer, temperature and the duration of the reaction also increase as well the degree of conversion in terms of ammonia and the yield of polyorganosilazasiloxanes, while their vitrification temperature decreases.

The polymerization polycondensation method turned out to be a sufficiently universal one for synthesizing polymers with inorganic and organo-inorganic macromolecular chains of various composition and structure, because it can employ organocyclosilazanes as well as organocyclosilsesquiazanes, mixed organocyclo-

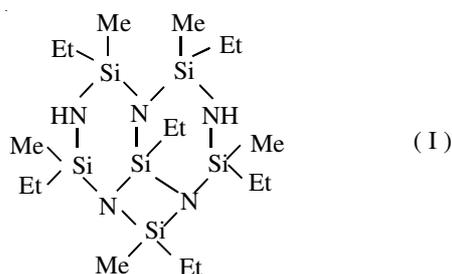
TABLE-1.4  
 CONDITIONS OF THE REACTION OF *TRIS*(TRICYCLODECENILMETHYL)-  
 CYCLOTTRISILOXANE WITH  $\alpha,\omega$ -DIHYDROXILIGODIMETHYLSILOXANE  
 AND SOME PROPERTIES OF THE OBTAINING POLYMERS

Structure of polymer elementary ring	Reaction temp. (°C)	Reaction time (h)	Amount of the separated NH <sub>3</sub> (%)	T <sub>g</sub> (°C)	Yield of the polymers (%)	$\eta_{red}$
$\left[ \begin{array}{c} \text{C}_{10}\text{H}_{13} \\   \\ \text{Si}-\text{NH} \\   \\ \text{Me} \end{array} \right]_2 - \begin{array}{c} \text{C}_{10}\text{H}_{13} \\   \\ \text{Si}-\text{O} \\   \\ \text{Me} \end{array} \left[ \begin{array}{c} \text{Me} \\   \\ \text{SiO} \\   \\ \text{Me} \end{array} \right]_{12}$	150-160	1.5	80	78	79	–
$\left[ \begin{array}{c} \text{C}_{10}\text{H}_{13} \\   \\ \text{Si}-\text{NH} \\   \\ \text{Me} \end{array} \right]_2 - \begin{array}{c} \text{C}_{10}\text{H}_{13} \\   \\ \text{Si}-\text{O} \\   \\ \text{Me} \end{array} \left[ \begin{array}{c} \text{Me} \\   \\ \text{SiO} \\   \\ \text{Me} \end{array} \right]_{32}$	170-180	2.5	85	100	82	–
$\left[ \begin{array}{c} \text{C}_{10}\text{H}_{13} \\   \\ \text{Si}-\text{NH} \\   \\ \text{Me} \end{array} \right]_2 - \begin{array}{c} \text{C}_{10}\text{H}_{13} \\   \\ \text{Si}-\text{O} \\   \\ \text{Me} \end{array} \left[ \begin{array}{c} \text{Me} \\   \\ \text{SiO} \\   \\ \text{Me} \end{array} \right]_{72}$	210-220	4.0	90	102	89	0.3

siloxanes, organocyclosiloxanes and organocyclosilsesquioxanes as the initial cyclic compound, which can readily entrain comparatively low reactionable different organic and organosilicon diols into polymerization polycondensation reaction.

Keeping in mind the dependence of the polymerization-polycondensation reaction on the structure and reaction ability of the original organosilicon heterocycles and diols, an investigation<sup>37</sup> was carried out into the interaction of polycyclic organocyclosilsesquiazanes with  $\alpha,\omega$ -dihydroxydimethylsiloxanes, dihydroxydiphenylsilane and tetrahydroxytetraphenylcyclotetrasiloxane (Tetrol).

The interaction of pentamethylhexaethyltricyclohexasilpentazane with the following structure:



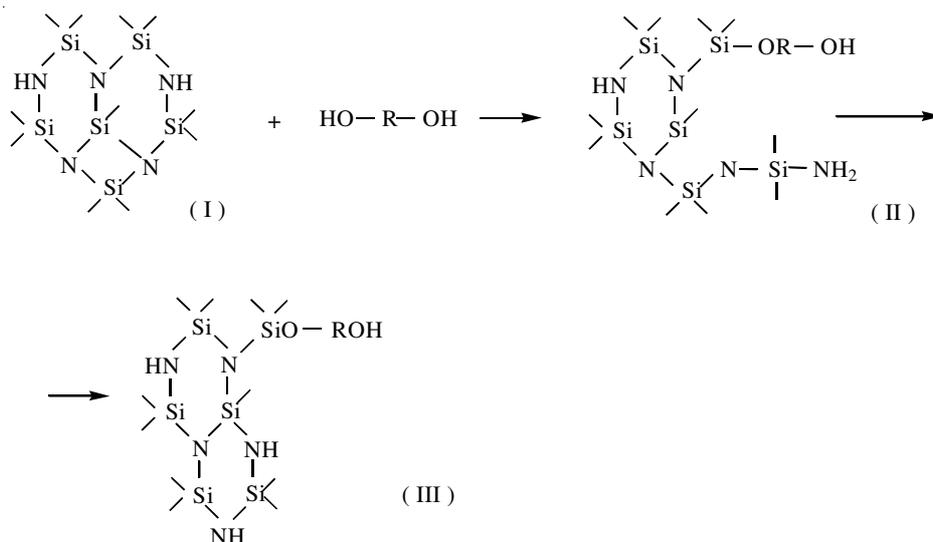
with  $\alpha,\omega$ -dihydroxyoligodimethylsiloxanes ( $n = 10.42$ ) and dihydroxydiphenylsilane in bulk at 170-180 °C and at an equimolar ratio of reagents<sup>38</sup>. It was shown that the reaction goes with ammonia isolation according to the combine polymerization polycondensation reaction scheme, however forming structurized polymers. Meanwhile, although of organocyclosilazanes and diols, it does not exceed 50 % when

diols react with a tricyclic compound **I**. In the latter case the initial stage of the reaction shows along induction period and as low growth of MM within the first 3-6 h. Here, just as in case of organocyclosilazanes, a silazane cycle opens initially along the Si-NH-Si bonds to form a Si-O bonds and terminal NH<sub>2</sub>-groups which starts a condensation reaction with the hydroxyl group of another diol molecule (**Scheme-1.11**).

Since a tri-cyclic compound contains two reaction centers in different cycles and each chemical event of opening a silazane ring gives rise to a new, more reactive NH<sub>2</sub>-group, there immediately appears a possibility of forming a branched oligomer with subsequent structurization. The reaction is slow one, limited by the stage of cycle openings. Only a prolonged heating of the reaction is a slow one, limited by the stage of openings of the cycle. Only a prolonged heating of the reaction at 220 °C and higher can facilitate an 85 % conversion in terms of ammonia and 85-86 % of the gel-fraction content (up to 60 % in case of dihydroxydiphenylsilane).

In contrast to the reaction of tricyclic compound **I** with organosilicon diols a three-dimensional polymerization polycondensation of cyclosilsesquiazane (T<sub>6</sub>) with α,ω-dihydroxyoligodimethylsiloxanes (n = 42) proceeds at a much higher rate. A great number of branching centres, 8 of them, in complex molecule of cyclosilsesquiazane (T<sub>6</sub>) ensures structurization of the system within 2 h at 150 °C and 10 min at 180 °C.

The polymerization-polycondensation reaction of complex cyclosilsesquiazane systems with organosilicon diols proceeding up to gel-formation, yields viscous, soluble liquids which after structurization form rubber-like substances, the vitrification temperature of shift to the negative temperature region and the elasticity modulus decreases with a longer siloxane chain.



**Scheme-1.11**

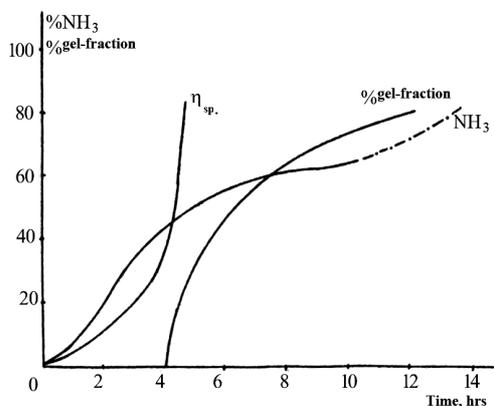
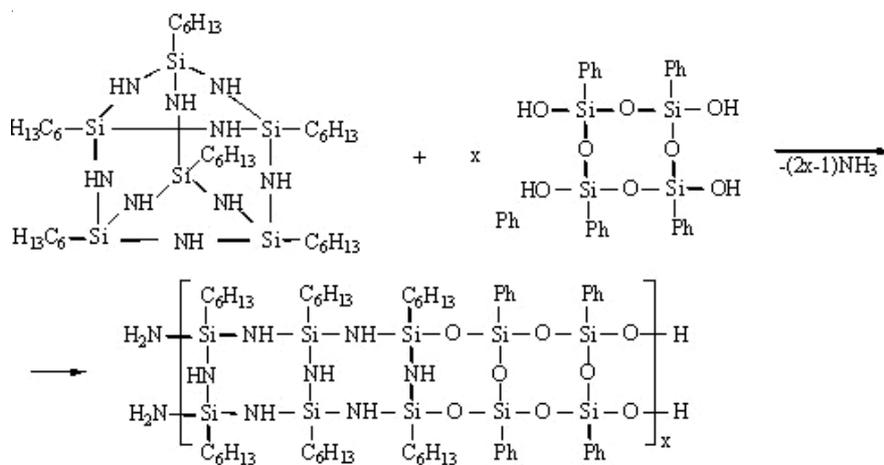


Fig. 1.7. Dependence of the amount of separated ammonia, specific viscosity (till gellation process) and gel fraction (%) on time in reaction of the pentamethyl-hexaethyltri-cyclohexasilpentazan with the  $\alpha,\omega$ -dihydroxidiphenylsilan in mass

An increase of functionality of the original hydroxyl-containing organosilicon compound from 2 to 4 in a polymerization polycondensation reaction does not lead to any increase in the three dimensional process rate and in the gel-fraction output. thus, the reaction of cyclosilsesquiazane  $T_6$  with tetrolproceeds under the same conditions (170-180 °C, reagents ratio 1:1) in block within 15 h with a 70 % conversion in terms of ammonia and *ca.* 15 % gel-fraction output. The reaction rate is much higher in a 40 % dioxane solution: at 95-100 °C the conversion in terms of ammonia reaches 93 % within 15 h, forming soluble products. Under cooling the solution precipitates crystalline substances (7-8 %) with  $T_m = 220-250$  °C, which are a mixture of octa- and decaphenylsilsesquiazanes  $T_8$  and  $T_{10}$ . these products being isolated and the solution removed, a polymer was obtained, its formation proceeds in the following way<sup>38</sup>:



Scheme-1.12



The nature of original diol influences greatly the course of this reaction, the structure and properties of the resulting products (Table-1.6).

Table-1.6 shows the polymerization polycondensation of  $\alpha,\omega$ -dihydroxyoligo-dimethylsiloxanes ( $n = 25$ ) with **I** in bulk and of diphenylpropane with **I**, both in bulk and in toluene, yields mainly insoluble products. When 1,2-*bis*(hydroxymethyl)-carborane reacts with **I**, a vitreous polymer, readily soluble in benzene and toluene. When *N,N'*-*bis*(hydroxydimethylsilyl)tetramethylcyclo-disilazane reacts with **I**, a soluble oligomer is formed. However, the conversion in terms of ammonia is not high either in bulk or in solution. The differences in the behaviour of the organic, carborane and organosilicon diols of different structures in the reaction with organospirobicyclosilazasiloxane can be explained by differences in the behaviour of nucleophilic molecules resulting from a side reaction between diol hydroxyl groups and the released ammonia, which catalyzes the further process of polymerization-condensation.

TABLE-1.6  
REACTION OF ORGANOSPIROBISCYCLOSILOXANE WITH VARIOUS DIOLS

Diol	Reaction conditions	Temp. (°C)	$\tau$ (h)	Amount of the evaluated $\text{NH}_3$ (%)	Gel-fraction (%)
$\text{HO} \left( \begin{array}{c} \text{Me} \\   \\ \text{---Si---O---} \\   \\ \text{Me} \end{array} \right)_{25} \text{H}$	In mass	180	5.0	70	66
$\text{HO} \text{---} \text{C}_6\text{H}_4 \text{---} \begin{array}{c} \text{Me} \\   \\ \text{---C---} \\   \\ \text{Me} \end{array} \text{---} \text{C}_6\text{H}_4 \text{---} \text{OH}$	In mass	150 110	6.5 3.5	86 90	73 31
$\text{HOH}_2\text{C} \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{CH}_2\text{OH}$ <div style="text-align: center;"> <math>\begin{array}{c} \diagdown \quad \diagup \\ \text{O} \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array}</math> </div>	Toluene	110	4.5	99	–
$\begin{array}{c} \text{Me} \\   \\ \text{HO} \text{---} \text{Si} \text{---} \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{Si} \\ \diagdown \quad \diagup \\ \text{Me}_2 \end{array} \text{---} \text{N} \text{---} \text{Si} \text{---} \text{OH} \\   \\ \text{Me} \end{array}$	In mass Toluene	140-200 110	4.0 9.5	48 40	– –

A lower acidity of carborane diol causes a leftward shift of an equilibrium reaction which forms a nucleophilic molecule and owing to a low concentration of nucleophilic molecules the siloxane cycle opens at an insignificant rate. However, the reaction of cycle opening with silazane groups and condensation of OH- and  $\text{NH}_2$ -groups is more complete (99 % conversion in terms of ammonia), thus forming a soluble polymer of a linear of weakly branched structure. The concentration of nucleophilic molecules that can open a siloxane cycle is higher in the reaction of silazasiloxane bicycle with dimethylsiloxane and aromatic diols due to rightward shift of the side reaction and to a less complete reaction resulting from a comparatively

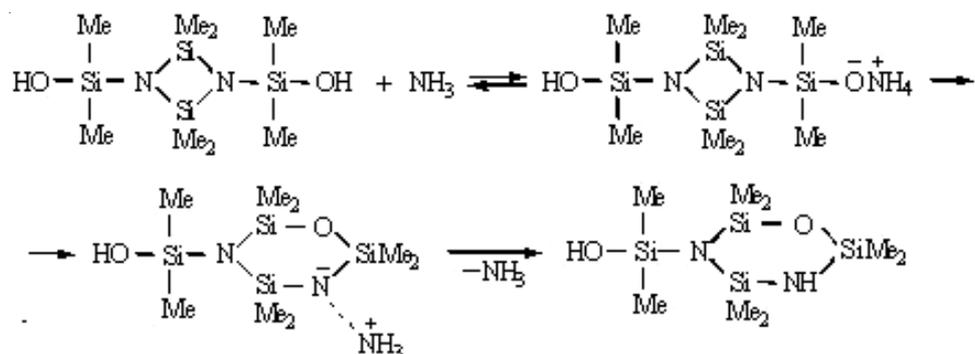
rapid formation of a branched and partial network polymer. Therefore, the experimental data prove the decisive role of the diol nature and bicyclosilazasiloxane cyclic activity in the formation of structured products.

An interesting reaction is observed during polymerization polycondensation of bicycle silazasiloxane with *N,N'*-bis(hydroxydimethylsilyl)tetramethylcyclodisilazane.

The reaction begins with opening silazane groups in the bicycle and condensation of formed terminal  $\text{NH}_2$ -groups with diol hydroxyl groups. However, as soon as ammonia appears in the reaction system, an anion regrouping of cyclodisilazane begins at a noticeable speed and with the cycle expansion (**Scheme-1.14**).

This result in the hydroxyl group concentration dropping and the reaction is less speedy and less complete, while the resultant polymers are of a lower MM.

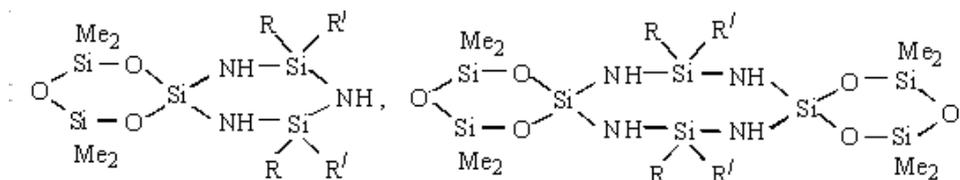
A similar re-grouping of cyclodisilazane accompanied by the cycle expansion and cyclodisilazasiloxane formation had been reported earlier by Andrianov *et al.* In a study of polymerization condensation of *N,N'*-bis(hydroxymethylsilyl)tetramethylcyclodisilane with dimethylcyclodisiloxanes in the presence of tetramethylammonium siloxanediolate<sup>39,47</sup>:

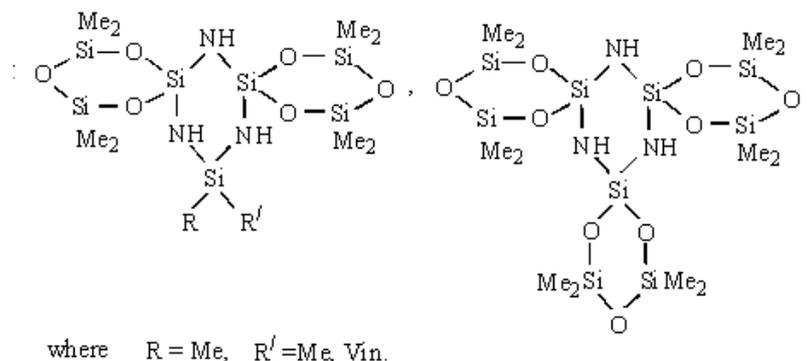


**Scheme-1.14**

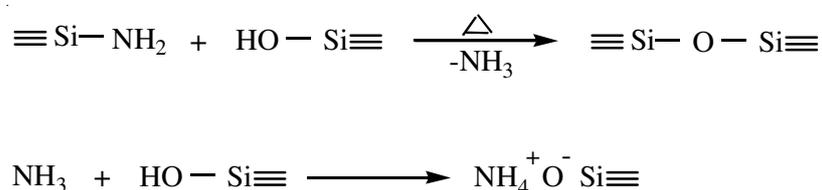
The polymers reported<sup>46</sup> are of a high thermal-oxidative stability. Their mass losses start at 350 °C and the basic destruction occurs at temperatures more than 400 °C.

It was investigated<sup>46</sup> the interaction of  $\alpha,\omega$ -siloxanediols with organospirocyclodisilazanes (SC) of a new type with following structures (**Scheme-1.15**):



**Scheme-1.15**

Here, two main processes are observed to proceed at 130-140 °C an opening of interior cycles occurs and the formation of oligomers with the SC structural fragments regularly arranged over the chain takes place: at 180-190 °C elastic polyorganosiloxanes (RP) of regular structure are obtained. The formation of RP is predetermined by the opening of cyclotrisiloxanic fragments and by the polymerization-exchange processes with the contribution of the nucleophilic particles type of  $\text{O}^-[\text{NH}_4]^+$  formed on the endings of the polymer chain, increasing the concentration (molar ratio) of isolating ammonia  $\text{NH}_3$ , due to heterofunctional polycondensation<sup>40</sup>:

**Scheme-1.16**

As it was established there is no requirement for initiators of ionic polymerization<sup>21</sup>.

On the basis of the determination of gel-fraction by the method of equilibrium swelling it was demonstrated that the density of cross-linking, together of RP essentially depends on the initial molar ratio of cyclosilazane:siloxandiol and achieves its maximum at a ratio corresponding to 1:1 of the components<sup>45</sup>.

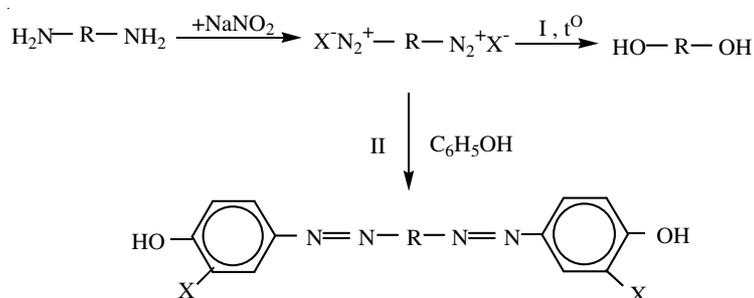
## 2. Polyorganosilazasiloxyheteroarylens and polyorganosilazasiloxazoarylens

It is known that incorporation of arylene groups into the main chain of polyorganosiloxanes leads to improvement of their thermal and mechanical properties<sup>22</sup>. It was expected that the analogous properties modification should take place in case of synthesis of the multi-functional polysilazasiloxyheteroarylens and

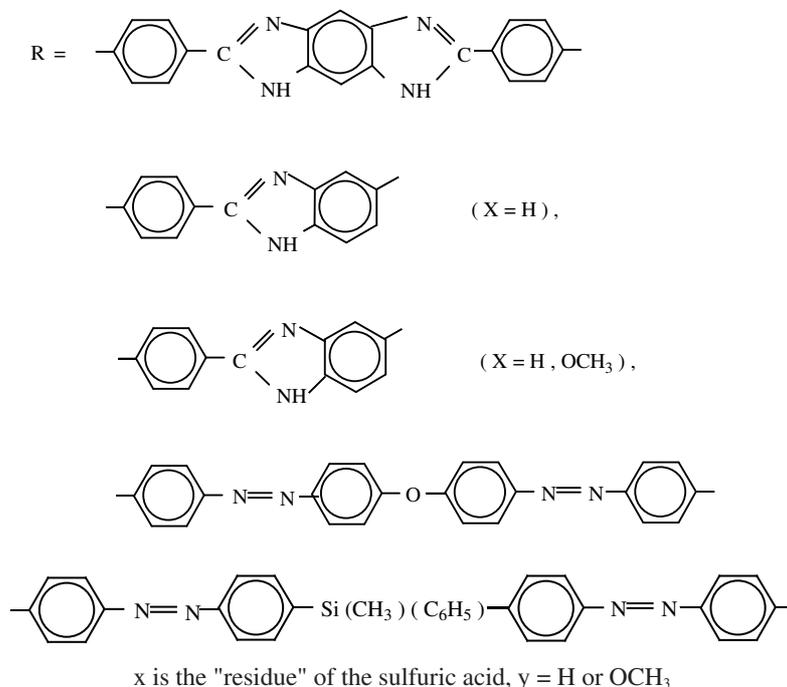
azoarylenes<sup>48-52</sup>. To obtain the polymers with the aforementioned structures the method of combined polymerization-condensation of silicon-nitrogen-containing heterocycles with heteroarylene and azoarylene bisphenols was used<sup>48,50</sup>.

As in the case of silazasiloxarilen polymers the choice of this method was justified by a row of the specific features, which gives the method clear advantages compared with the other methods of synthesis of the silicon-organic polymers with the organic-inorganic main chains<sup>48,50</sup>.

As the silicon-nitrogen-containing heterocycles, the reaction-able organocyclo-trisilazanes with different organic radicals at the silicon atom were used:  $[R' R'' SiNH]_3$ ,  $[R' = R'' = CH_2, R' = CH_2, R'' = CH=CH_2, C_{10}H_{13}, (dicyclopentadienyl)]^{48}$ ,  $C_6H_5^{49}$ .



where:



**Scheme-2.1**

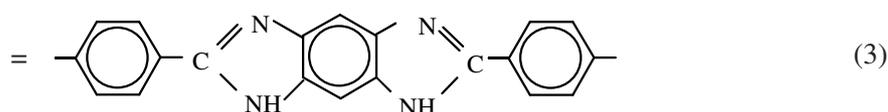
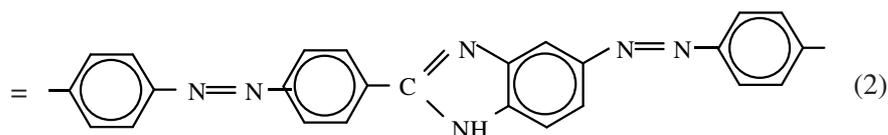
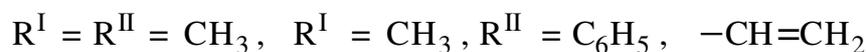
As the initial heteroarylene and the azoarylene bisphenols, the compounds, obtained transformation of corresponding diamines according to the reaction scheme (**Scheme-2.1**)<sup>49</sup>, were used. The obtained bisphenols are coloured crystalline substances with a high melting point (> 180 °C). The bisphenols composition and structure were estimated by using the elemental analysis and the IR and UV-spectroscopy<sup>49</sup>: in the IR-spectra, the absorbency bands corresponding to the imideazole cycles (1450-1425 cm<sup>-1</sup>) were found along with the absorbency bands corresponding to the OH-groups (3600-3500 cm<sup>-1</sup>). The band corresponding to the NH<sub>2</sub>-group (3400-3300 cm<sup>-1</sup>), in the IR spectra was not found. In the UV-spectra of the bisphenols type II (**Scheme-2.1**), the λ<sub>max</sub> = 345-360 nm characteristic to the -N=N- groups<sup>50</sup> were found.

The structure and some properties of synthesized bisphenols are presented in the Table-2.1.

The general reaction scheme of the combined polymerizing of organocyclo-trisilazanes with hetero- and azoarylene bisphenols analogous to the reaction with the "simple" aromatic diols (resorcin, "dian", naphtholdiols)<sup>48</sup> can be represented as shown below (**Scheme-2.2**):



where:



**Scheme-2.2**

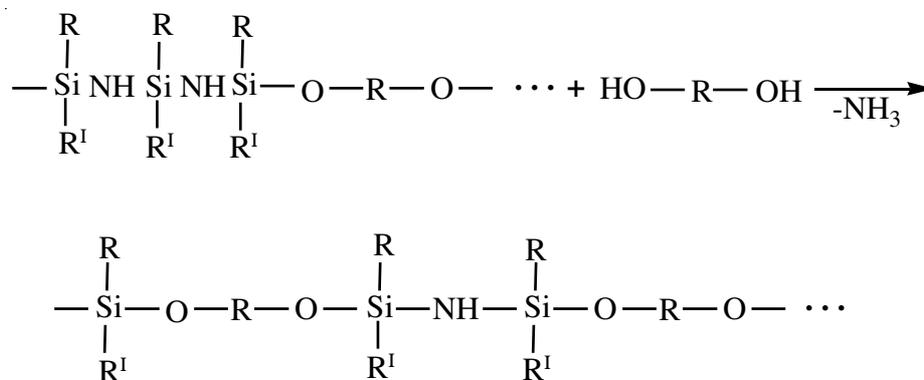
TABLE-2.1  
H YIELD AND SOME CHARACTERISTICS OF HETEROARYLEN AND -AZOARYLEN BISPHENOLS

No.	Formula	Yield (%)	m.p. (°C)	N <sub>exp.</sub> (%)	OH <sub>exp</sub>	M <sub>calc.</sub> /M <sub>det.</sub> (by determ of OH-groups)
1		80	183-184	11.53	8.2	410/419
2		78	205-206	12.26	8.3	408/409
3		87	180-181	16.90	6.8	-
4		89	262	12.21	-	-
5		91	268	19.13	-	-

TABLE-2.2  
 CONDITIONS OF SYNTHESIS AND SOME PROPERTIES OF POLYORGANOHETEROARYLENS AND -AZOARYLENS

No.	Cyclosiloxane	Bisphenol	React. temp. (°C)	React. time (h)	Polymer specific viscosity, $\eta$ (dl/g)	Yield of polymer by isolated NH <sub>3</sub> (%)	Si, Exp./Teor.
1	[(CH <sub>3</sub> ) <sub>2</sub> SiNH] <sub>3</sub>		160	9	0.26	93.8	11.79/ 12.46
2	[CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> SiNH] <sub>3</sub>		160	10	0.17	92.0	9.1
3	[CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> SiNH] <sub>3</sub>		160	12	0.19	90.0	9.01
4	[CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> SiNH] <sub>3</sub>		180	8	0.22	89.0	11.27/ 13.6
5	[(CH <sub>3</sub> ) <sub>2</sub> SiNH] <sub>3</sub>		180	8	0.20	92.0	18.84/ 19.8
6	[CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> SiNH] <sub>3</sub>		180	8	0.28	94.6	-

To obtain the polymerizing condensation process basic regularities, the reaction was conducted both in oil and in the amide aprotic solvents (N,N-methylpyrrolidone) in the media of dry argon. The reaction in the volume intensely occurs at 150-160 °C. In solvents, the reaction temperature is close to the solvents boiling temperatures. The choice of a certain temperature regime for the reaction is mainly based on the structure of the organic radical at the silicon atom. For example, the polymerizing condensation of trimethyltriphenylcyclotrisiloxane with bisphenols was conducted at 160-180 °C. In the case of conducting the reaction in the volume, the complete homogenization of the reaction mass is observed after the quantitative separation of ammonia. It should be noted that the chain composition of the preparing polymers (based on the Si content, %) are slightly different if the reaction is conducted in the volume or in the solution. In particular, for the polymer based on  $[\text{CH}_3(\text{C}_6\text{H}_5)\text{SiNH}]_3$  and heteroarylene bisphenol (**1**) (**Schemes 1.1, 1.2, 1.3**), the silicon content of polymer obtained at the reaction in the volume is 11.2 %, which is lower compared with the silicon content of the polymer obtained in solution N,N'-dimethylformamide (13.1 %). This can be possibly connected with the statistical process of substitution of the residual bisphenol in forming macrochains of the polysilazane polymer on the SiNHSi bonds simultaneously with the molecular mass increase of the polymerizing condensation product (**Scheme-2.3**)<sup>22,48</sup>:



Scheme-2.3

The possibility of occurring of the side of the residual bisphenol in the polysilazane chain substitution is confirmed by formation of polymers close on structure to the polysiloxyhetero-arylene and azoarylene structures obtained at interaction of organocyclotrisiloxanes with bisphenol tri-mole excess<sup>50</sup> (**Scheme 2.4**).

$n/3[\text{CH}_3\text{R}'\text{SiNH}]_3 + n\text{HO-R-OH} \rightarrow \text{H}_2\text{N}(\text{Si}(\text{CH}_3)\text{R-O-R-O})_n\text{H} + (2n-1)\text{NH}_3$ ,  
 where  $\text{R}' = \text{CH}_3$ , R is the bisphenol "residue"

Scheme-2.4

However, the 100 %-substitution of the "residual" voluminous and stiff-chain bisphenols does not occur which was confirmed by the IR-spectra. The weak absorbency bands in the range 940-930  $\text{cm}^{-1}$  corresponding to the Si-NH-Si groups<sup>50</sup> were found.

In conducting the reaction of organocyclotrisiloxanes with bisphenols (in the volume), it was found that in the same experiment conditions and with the same bisphenol, the reaction rate (based on  $\text{NH}_3$  separation) depends on the nature of the organic radical and its maximal value was observed in the case of hexamethylcyclotrisilazane (Fig. 2.1).

This is, probably, the result of not only the small volume of the methyl radicals at Si-atom but also of the electron-acceptor effect of the phenyl groups. The last effect causes the strengthening of the conjunction of the silicon *d*-electrons with the nitrogen  $\pi$ -electrons which would increase the strength of the Si-N-bond toward the influence of the bisphenol hydroxyl-groups<sup>22,24</sup>. It should be noted that for this particular reaction, the existence of the induction period is observed (Fig. 2.1). Its longevity depends, basically, on the volume and the electron nature of the organic frame around the silicon-atom<sup>50</sup>. The analogous phenomenon is observed in case of the combined polymerization condensation of organocyclotrisiloxanes with the "sample" aromatic diols and probably, it is connected with formation of the temporary complex type A (**Scheme-1.6**)<sup>50</sup> and its consecutive decomposition on the linear oligomers with the end groups  $\text{NH}_2$ - and -OH. Further on, the groups interact either with the organosiliconheterocycle or with themselves or with bisphenol with separating ammonia (**Scheme-2.2**)<sup>48,50</sup>.

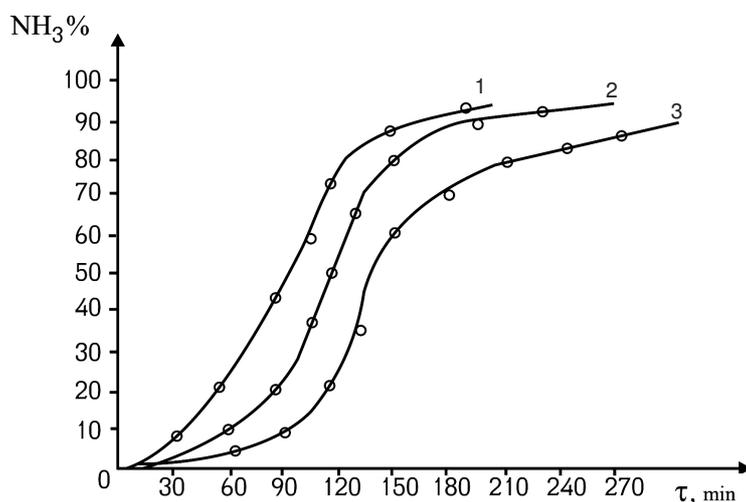


Fig. 2.1. Dependence of the ammonia amount separated on time,  $t$ , in the following reactions (1:1 ratio), temperature 160 °C; (1)  $[(\text{CH}_3)_2\text{SiNH}]_3 + \text{Bisphenol-2}$ ; (2)  $[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{SiNH}]_3 + \text{Bisphenol-2}$ ; (3)  $[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{SiNH}]_3 + \text{Bisphenol-1}$  (1:1) (Table-2.8)

Based on the IR-spectra, the conductance of the branching reaction, the formation of the trisilazane substituted nitrogen atom, which may be formed in the reaction of the terminal  $\text{NH}_2$ -groups of the intermediate oligomeric products with the  $\text{NH}$ -groups of the propagating chain, does not occur<sup>50</sup>.

An interesting experimental fact was observed in conducting the reaction of the hexa-methylcyclotrisiloxane with heteroarylene bisphenols having different structure. In particular, in forming polymers by interaction of  $[\text{CH}_3(\text{C}_6\text{H}_5)\text{SiNH}]_3$  with bisphenol-B, the character of the intrinsic viscosity increase in the process is significantly is different. In the case of the reaction with bisphenol-B the viscosity increases more uniformly. This can be probably explained by the different reaction ability of the  $\text{OH}$ -groups of bisphenol-A (by the distribution of the particular charges on the corresponding carbon atoms, Fig. 2.2).

By the analysis of the obtained data and also in accordance with the model reaction<sup>50</sup>, the system of differential equations was prepared. The system describes the certain mechanism of the investigating reaction. Based on the theoretical calculations<sup>50</sup>, several possible reaction mechanisms were suggested to choose from. At the given preciseness of the experiment, the most satisfactory (the minimal average deviation) (Fig. 2.2) mechanism corresponding to the scheme shown above (Scheme-1.6):

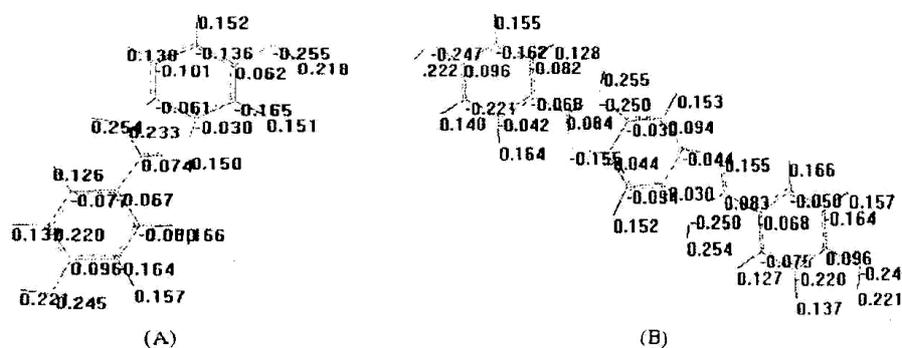


Fig. 2.2. Quantum-chemical calculations of distribution of the particular charges on the atoms in the molecule of bisphenol-A and bisphenol-B

The reaction transamination is less probable due to the low intermediate concentration of the  $\text{Si-NH}_2$ -groups and the higher activation energy,  $E_a$  compared with the reaction of the hetero-functional polycondensation<sup>50</sup>.

It should be noted that it is possible some deviation from the "ideal" scheme of the reaction of bisphenol with  $\text{Si-NH-Si}$ -bonds of the propagating chain. However, to take this into account is difficult in solving the calculation tasks<sup>48</sup>.

The obtained polymers are ones soluble in aprotic solvents, glassy solids, resin-like or powder-like products having  $\eta_{sp} = 0.17\text{-}0.28$  dl/g and the yield 89-94.5 % (according to the separating ammonia).

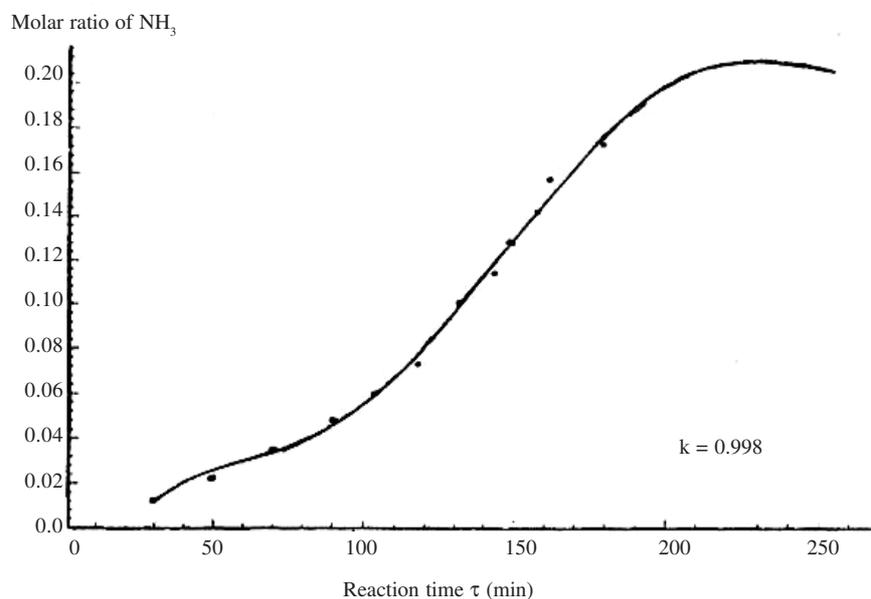


Fig. 2.3. Comparison of the theoretical curve (solid line) and the experimental data (points) of the dependency of the separated ammonia on the time of reaction  $t_n$  of  $[(\text{CH}_3)(\text{C}_6\text{H}_5)\text{SiNH}]_3 + \text{bisphenol-B (1:1)}$

### 3. New type Si-N containing polymers with organic-inorganic main chains

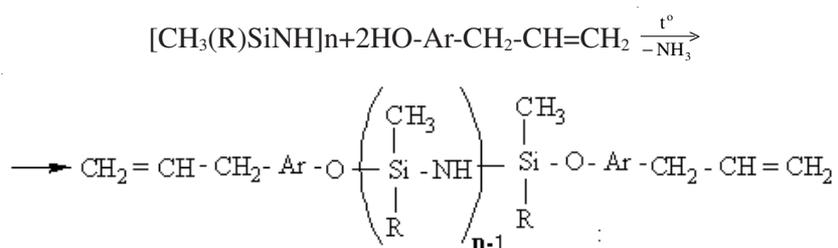
During the previous years the synthesis of heterochain silicon-organic monomers and polymers (silazane, siloxane-arylene, carbosilazane, epoxide, *etc.*), containing aromatic groups with unsaturated radicals of allyl and vinyl types, have been attracting particular attention<sup>53-56</sup>. To obtain the polymers with such structure, the classical method of the polyhydrosilylation revealed new possibilities. The range of unsaturated monomers used for reaction of polyhydrosilylation increased<sup>54</sup>. The use of unsaturated monomers of the new type, distinguished from the standard divinyl monomers, required elaboration of a non-traditional approach to this reaction<sup>54</sup>. On the other hand, the synthesis of the polymers with the aforementioned structure is of interest for modification of properties of some important industrial polymers, such as polycarbonate, phenolformaldehyde gums, rubbers based on carbochain and siliconorganic elastomers, *etc.* They may be also used in combination with some other organic and element-organic polymers (for example with polyepoxides) as the substrates for nano hybrids<sup>55</sup>.

For the synthesis of new dialyl silazane monomers the condensation method has been used for the synthesis of the polymers based on the polyhydro-silylation method. The cyclotrisiloxanes were synthesized by the ammonolysis of corresponding dichlorine silanes.  $\alpha,\omega$ -Oligodimethyldihydridsiloxanes were synthesized by the described methods<sup>56</sup>. 1,3-tetramethyldisiloxane was obtained by hydrolysis of

dimethylchlorinesilane<sup>54,55</sup>. 1,5-Trimethyltriphenyltrisiloxane has been synthesized by reduction of 1,5-dichlorine-1,3,5-trimethyltriphenyl-trisiloxane with LiAlH<sub>4</sub><sup>30</sup>. 1,5-tetramethyl-3,3-diphenyltrisiloxane was obtained *via* interaction of (Me)<sub>2</sub>SiHCl with diphenylsilandiol<sup>54,55</sup>.

We have conducted polyhydrosilylation reactions of  $\alpha,\omega$ -dihydrooligo-organosiloxanes and 1,4-bis(dimethylsilyl)benzene with dialylsilazanes (DAS) in the presence of Speier's catalyst (0.1 mole solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in isopropanol)<sup>55</sup> in dry toluene in mass ratio.

The initial dialylsilazanes were synthesized *via* reaction of commercial organocyclosilazanes (hexamethylcyclotrisiloxane, methylphenylcyclotrisiloxane and methylvinylcyclotrisiloxane) with *ortho*-allylphenol (*o*-AP) and 4-allyl-2-methoxyphenol (Evg.), in dry argon. The reactions proceeded easily at 60-80 °C according to the following **Scheme 3.1**<sup>55</sup>:



where R = CH<sub>3</sub>, CH=CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>, Ar = phenylene, methoxyphenylene, n = 3

### Scheme-3.1

In early work<sup>22</sup> it was reported that in reactions of cyclosilazanes with allylphenols the induction period is significant. This fact was explained by formation of a transition complex (**A**) that later decomposes and produces a linear allylsilazane with terminal amino-groups (**B**)<sup>22</sup>. Then **B** is believed to react with another allylphenol molecule generated from DAS<sup>22</sup>.

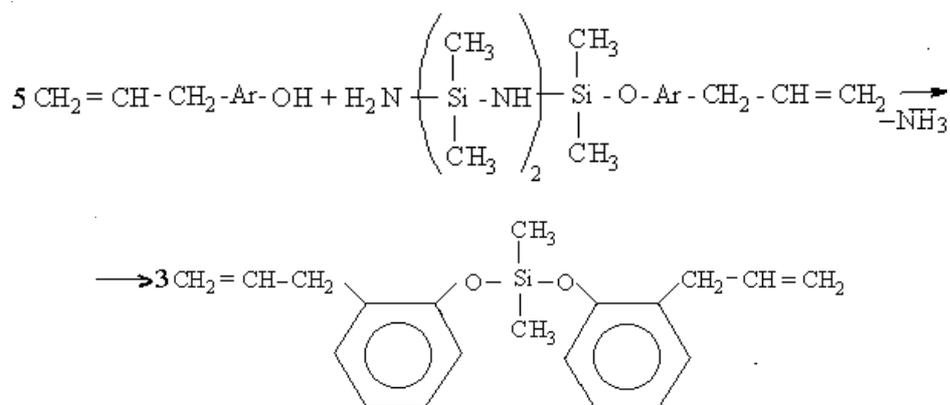
We have used a simple model system of phenol with organocyclosilazanes<sup>22</sup> to determine feasible mechanism of the reaction. It is believed that the reaction involves a more complicated mechanism. Alongside with the stages of obtaining the transition complex and of opening silazane cycle, there may be two side processes: formation of trisilylated nitrogen atom due to interaction of the terminal amino group of intermediate aminoallylphenoxisilazanes with Si-NH-Si groups of silazane heterocycles and the stage of *trans*-amination. In fact, earlier we<sup>22</sup> have suggested the following reaction:



A comparison of theoretical curve of formation of ammonia and experimental kinetic data on the reaction of phenol with organocyclosilazane in mass confirmed the feasibility of the reaction mechanism already proposed<sup>22</sup>.

Based on earlier results of calculations of rate constants of the elementary stages we can now show that the limiting stage of the reaction is formation of the transition complex (**A**) giving rise to the induction period<sup>22</sup> and opening of silazane cycle. Returning to the rate constants of the main and side stages (Table-3.1) of the reaction, it is concluded that the probability of the side stages of formation of trisilylated nitrogen atom and *trans*-amination is low. In real systems, the reaction of branching of linear silazane chain due to interactions of terminal amino group of intermediate aminoallylphenoxy silazanes with Si-NH-Si groups of DAS would take place only at relatively high temperatures-as suggested in previous work<sup>56</sup>. In conditions of the reaction, formation of triallylsilazane was not found. Thus, in the IR spectra of the reaction products the maximum absorption related to the trisilylated nitrogen atom was not observed<sup>54</sup>.

It is noted that carrying out the reaction of hexamethylcyclotrisilazane with allylphenols in the molar ratio 1:6 leads to formation of *bis*(allylphenoxy)dimethylsilane according to the following **Scheme 3.2**<sup>55</sup>:



**Scheme-3.2**

The resultant products are slightly viscous, optically transparent (in visible region of the spectra), soluble in typical organic solvents (benzene, toluene, acetone, *etc.*) and practically insoluble in water. The composition and structure of the obtained *bis*(allylphenoxy)diorganosilazanes and silanes were confirmed, before based on the data of elemental and IR spectral analysis<sup>56</sup>.

The IR spectra of all samples were obtained with SPECORD and UR-20 spectrophotometers, from KBr pellets, while the <sup>1</sup>H NMR spectra were obtained with AM-360 instrument at the operating frequency of 360 MHz. All spectra were obtained by using CDCl<sub>3</sub> as solvent and an internal standard. The Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine DTA and the thermal (phase)

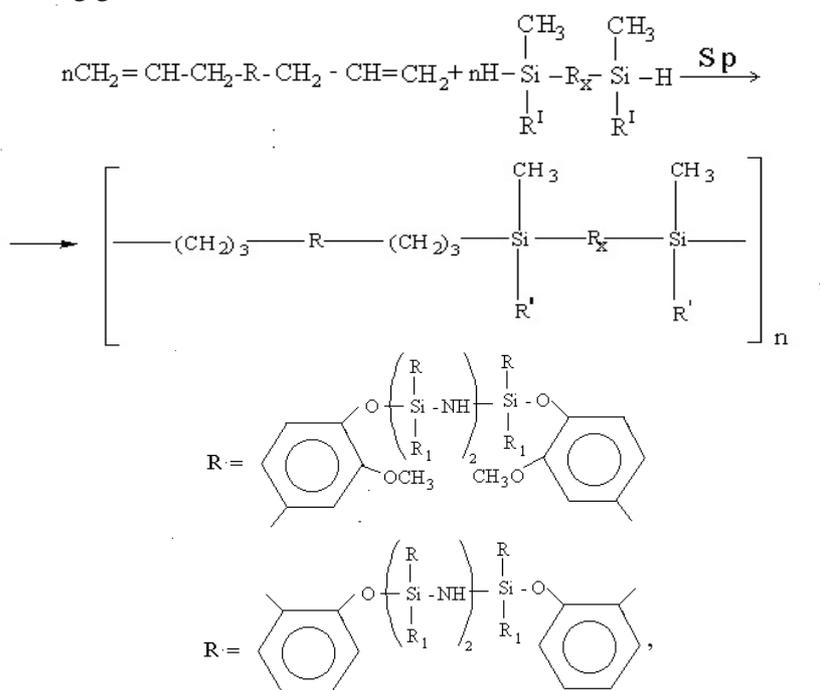
transition temperatures were recorded endothermic or exothermic peaks. Heating and cooling scanning rates were 10 °C/min. The column set comprised 10<sup>3</sup> and 10<sup>4</sup> Å Ultrastyrigel columns. Wide-angle X-ray diffractograms were obtained with DRON-2 instrument. CuK<sub>α</sub> was measured without a filter and the angular velocity of the motor was ω ≈ 2 °/min

The IR spectra show maxima of absorption related to Si-NH-Si and Si-O-Si, Si-O-C groups (925-915, 1000-990 and 1080-1060 cm<sup>-1</sup>). Also there are maxima of the absorption related to Si-CH<sub>3</sub>, CH<sub>2</sub>=CH, Si-C<sub>6</sub>H<sub>5</sub> and benzene link (1250, 1430, 1445, 1630-1620, 1605-1600 cm<sup>-1</sup>, respectively)<sup>56</sup>.

IR spectra of *bis*(allylphenoxy)dimethylsilane (**Scheme-3.4**) did not reveal the presence of the absorption related to Si-NH-Si groups<sup>56</sup>.

As we have noted of our method of manufacturing previous work<sup>6</sup>, diallyl-silazanes is easily performed and has some noteworthy positive technological features for a practical viewpoint<sup>56</sup>: (a) The reaction is carried out in the absence of solvents and catalysts; (b) Removal of side products is not difficult; (c) Control of the process is simple due to determination of the gaseous ammonia.

Polyhydrosilylation reactions of 1,4-*bis*(dimethylsilyl)benzene and α,ω-dihydroorganosiloxanes with dilsilazanes so synthesized can be represented by the following general **Scheme-3.3**<sup>56</sup>:



where R<sub>x</sub> = O, C<sub>6</sub>H<sub>4</sub>, O[Si(CH<sub>3</sub>)<sub>2</sub>O]<sub>m</sub>, (m = 6,11), CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)SiO, Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, R = R<sub>1</sub> = CH<sub>3</sub>; R = CH<sub>3</sub>, R<sub>1</sub> = CH=CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>; n >> 1.

**Scheme-3.3**

We have determined active hydrogen in Si-H groups several times as reported earlier<sup>47</sup>. Influence of the structure of dihydride monomers on the reaction rate, yield and properties of obtained polymers has been thus evaluated. The results are presented in Table-3.1 and Fig. 3.1. Based on kinetic curves of Si-H groups conversion, the reaction rate constants have been determined (Table-3.1). The total reaction order is equals to 2.

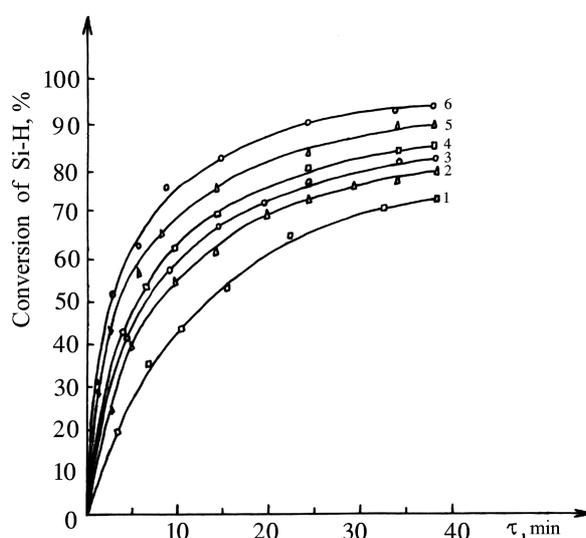


Fig. 3.1. Conversion of Si-H group in time for hydrosilylation reaction of  $\alpha,\omega$ -dihydrooligo-organosiloxanes and 1,4-*bis*(dimethylsilyl)benzene with diallylsilazanes: (1) VII; (2) VI; (3) III; (4) II; (5) V; (6) IV (Table-3.1)

Products of polyhydrosilylation reaction are optically transparent viscous liquids or elastic gums soluble in ordinary organic solvents (toluene,  $\text{CHCl}_3$ , *etc.*).

Composition and structure of polysilazanes so produced were from elemental IR and  $^1\text{H}$  NMR spectral analyses. In IR spectra, we have found the absorptions (925-915, 1000-990, 1060-1020, 1250, 1410, 1430, 1445, 1605-1600  $\text{cm}^{-1}$ ), related to Si-NH-Si, Si-O-Si, Si-O-C<sub>ar</sub>, Si-CH<sub>2</sub>, Si-CH<sub>3</sub>, Si-C<sub>6</sub>H<sub>5</sub> and benzene link, correspondingly (**Scheme-3.1**). Results of elemental analysis (for example, Si(I), %, calc./found = 17.01/16.08; Si(VIII), %, calc./found. = 17.84/17.09, *etc.*, where the index numbers I and VIII the numbers of polymers in the Table-3.1) correspond to the structures of the products obtained in agreement with the reaction **Scheme-3.2**.

It is observed that the singlet signals with chemical shifts within the range of  $\delta \approx 0.03$ -0.44 ppm for protons in methyl group of  $\equiv\text{Si-CH}_3$  in  $^1\text{H}$  NMR spectra of the synthesized polymers (there illustrated the data for IV and VI-Table-3.1). We also observe two signals with centers of chemical shifts at 1.28 and 1.62 ppm which correspond to methylene protons in Si-CH<sub>2</sub> groups. There are also multiplet signals

with chemical shifts in the range of  $\delta \approx 6.6-7.5$  ppm corresponding to protons of phenyl groups in the  $^1\text{H}$  NMR spectra. Further, we have observed the signals with chemical shifts in the range of  $\delta \approx 5.1-5.2$  ppm corresponding to protons in NH-groups in  $^1\text{H}$  NMR spectra. The triplet signals with center of chemical shifts at 0.81 ppm correspond to methine protons in Si-CH(CH<sub>3</sub>) groups<sup>55</sup>.

Thus, our (elemental and spectral analysis and product solubility results) exclude homo-polymerization of diallylsilazanes under the conditions of polyhydrosilylation reaction.

To evaluate the relative reactivity of dihydrosiloxanes (determination of the rank of their relative reactivity in polyhydrosilylation reaction), an algebraic-chemical method have been used based on pseudo-ANB-matrices. This is the first time this method has been used for these type reactions. This is a modified version of adjacency matrices<sup>57</sup> and we take into account the nature (structure) of organic radicals R and R<sup>1</sup> at the silicon atoms of the dihydride siloxanes. Gverdsiteli and coworkers have demonstrated that log(DANB) is a convenient index for quantitative structure-property relations<sup>53,56</sup>. Here DANB is the corresponding correlation equation has the following form:  $\mathbf{k} = \mathbf{alg}(\Delta_{\text{ANB}}) + \mathbf{b}$  ( $\mathbf{k}$  is a rate constant for polyhydro-silylation reaction. The determinant of pseudo-ANB-matrices;  $\mathbf{a}$  and  $\mathbf{b}$ -slope and intercept, which are calculated by method of least-squares:  $\mathbf{a} = 6.792 \times 10^{-3}$ ,  $\mathbf{b} = 3.083 \times 10^{-3}$ . The correlation coefficient  $r = 0.9788$  (Fig. 3.2).

As noted in earlier works<sup>54,55</sup>, polyhydrosilylation reaction of dihydrosiloxanes with  $\alpha,\omega$ -divinyloligoorganosiloxanes proceeds according to the **Scheme-3.3**. However, recent publications<sup>55,57</sup> show that both  $\alpha$  and  $\beta$  adducts (products of the hydride addition reaction according to anti-Markownikov and Markownikov rule) are obtained (**Scheme-3.4** below).

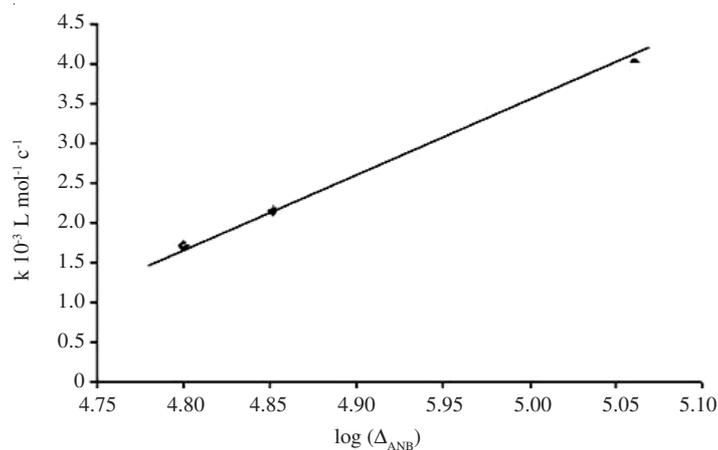


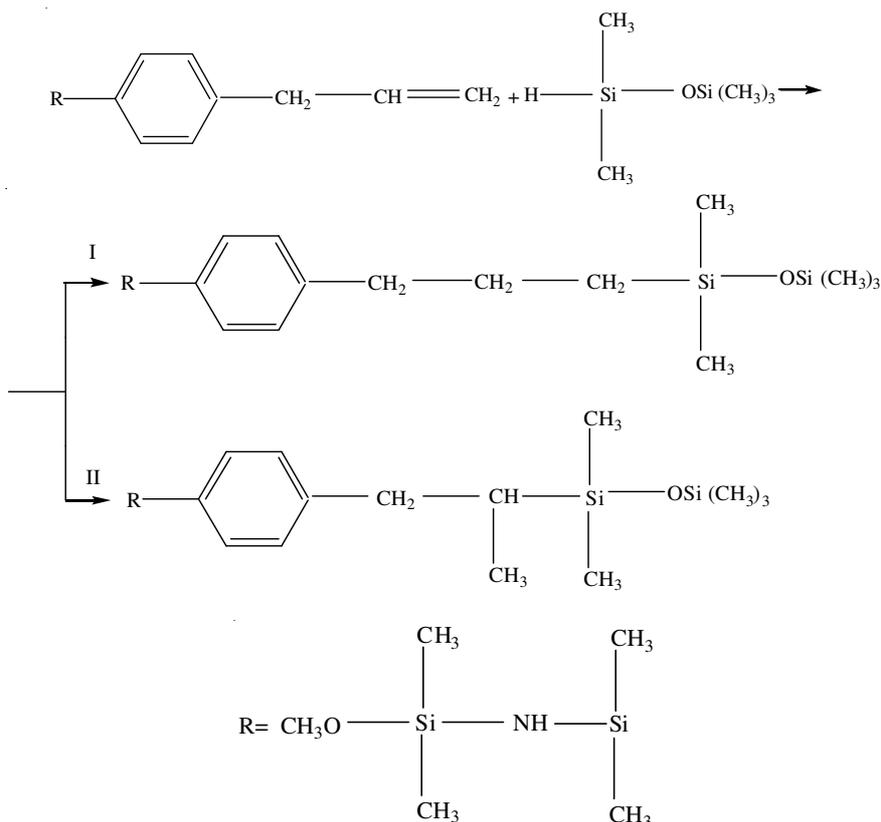
Fig. 3.2. Dependence of  $k$  value for hydrosilylation reaction rate constants on decimal logarithm of determinants of pseudo-ANB-matrices in the series of  $\alpha,\omega$ -dihydro-oligoorganosiloxanes (Table-3.1)

TABLE-3.1  
 CONDITIONS OF HYDROSILYLATION REACTION OF 1,4-*bis*(DIMETHYLSILYL)-  
 BENZENE AND  $\alpha,\omega$ -DIHYDROOLIGOORGANOSILOXANES WITH  
 DIALLYLSILAZANES (DAS)\*, THE YIELD AND VALUES OF SPECIFIC  
 VISCOSITIES OF SYNTHESIZED POLYMERS (IN TOLUENE)

**	$\alpha,\omega$ -Dihydrideoligoorgano-siloxanes and 1,4- <i>bis</i> (dimethylsilyl)benzene	Reaction temp. (K)	Reaction time (h)	Yield of products of the reactions (%)	$\eta_{sp}^{***}$	Poly addition reaction rate constants $k \times 10^{-3}$ ( $L \text{ mol}^{-1} \text{ s}^{-1}$ )
I	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{H}-\text{Si}-\text{O}-\text{Si}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	333	12	96.6	0.17	—
II	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{H}-\text{Si}-\text{C}_6\text{H}_4-\text{Si}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	333	10	85.5	0.10	2.29
III	$\begin{array}{c} \text{CH}_3 \quad \text{C}_6\text{H}_5 \quad \text{CH}_3 \\   \quad   \quad   \\ \text{H}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{H} \\   \quad   \quad   \\ \text{CH}_3 \quad \text{C}_6\text{H}_5 \quad \text{CH}_3 \end{array}$	333	12	97.0	0.21	2.78
IV	$\begin{array}{c} \text{CH}_3 \quad \left( \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O} \\   \\ \text{CH}_3 \end{array} \right) \quad \text{CH}_3 \\   \quad \quad \quad   \\ \text{H}-\text{Si}-\text{O}-\quad \quad \quad \text{Si}-\text{H} \\   \quad \quad \quad   \\ \text{CH}_3 \quad \quad \quad \text{CH}_3 \end{array}$ <p style="text-align: center;">6</p>	333	12	96.4	0.13	4.33
V	$\begin{array}{c} \text{CH}_3 \quad \left( \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O} \\   \\ \text{CH}_3 \end{array} \right) \quad \text{CH}_3 \\   \quad \quad \quad   \\ \text{H}-\text{Si}-\text{O}-\quad \quad \quad \text{Si}-\text{H} \\   \quad \quad \quad   \\ \text{CH}_3 \quad \quad \quad \text{CH}_3 \end{array}$ <p style="text-align: center;">11</p>	333	12	91.7	0.22	3.97
VI	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\   \quad   \quad   \\ \text{H}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{H} \\   \quad   \quad   \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	333	12	96.2	0.15	2.38
VII	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{H}-\text{Si}-\text{O}-\text{Si}-\text{H} \\   \quad   \\ \text{C}_8\text{H}_{17} \quad \text{C}_8\text{H}_{17} \\ \text{CH}_3 \quad \text{C}_6\text{H}_5 \end{array}$	333	12	94.6	0.11	1.54
VIII	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\   \quad   \quad   \\ \text{H}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{H} \\   \quad   \quad   \\ \text{CH}_3 \quad \text{C}_6\text{H}_5 \quad \text{CH}_3 \end{array}$	343	12	93.4	0.12	—

\* $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Ar}-\text{O}[(\text{CH}_3)_2\text{SiNH}]_2(\text{CH}_3)_2\text{SiO}-\text{Ar}-\text{CH}_2-\text{CH}=\text{CH}_2$ ; where Ar =  $\text{C}_6\text{H}_4$  (VIII); Ar =  $\text{CH}_3\text{OC}_6\text{H}_4$  (I-VII) (**Scheme-2**); \*\*The Latin numerals in the leftmost column identify both the monomers and their polymers; \*\*\* 1 % Solution in toluene.

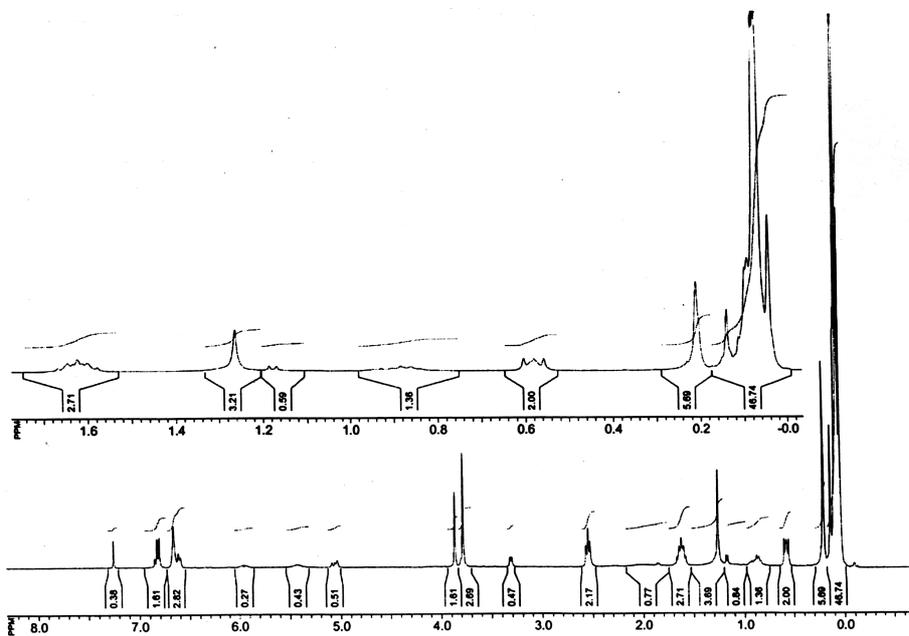
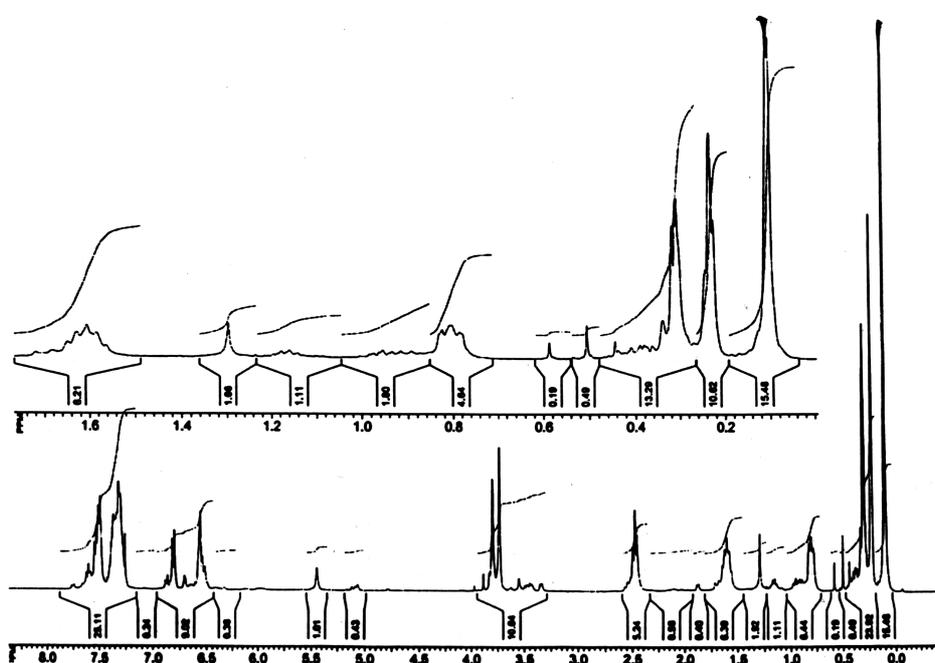
Quantum-chemical calculations of heats of formation of the model systems (**Scheme-3.4**), which are similar to the actual structures, have confirmed that polyhydrosilylation reaction proceeded according to the aforementioned two concurrent directions:



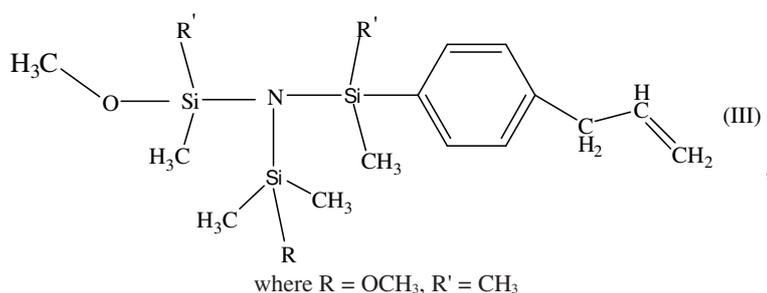
**Scheme-3.4**

As a method of quantum-chemical calculation, we used AM1 method<sup>35</sup>, the computation keywords used in this study were the following: EF GNORM = 0.100 MMOK GEO-OK AM1. For simplicity, preliminary geometry optimization of the investigated species was performed by using molecular mechanics (MM2 force field<sup>55,57</sup>).

We have thus calculated the enthalpies of formation  $\Delta H_{\text{form}}$  for the reaction model products. The results show that formation of the  $\alpha$ -adduct (I) ( $\Delta H_{\text{form}}^{\text{I}} = -1068$  kJ/mol) is slightly more probable than that of the  $\beta$ -adduct (II) for the product with the structure II,  $\Delta H_{\text{form}}^{\text{II}} = -1056$  kJ/mol. We have shown<sup>53</sup> that in both I and II products are actually obtained. Signals for chemical shifts at  $\delta = 0.81$ - $0.82$  and  $\delta = 1.61$ - $1.63$  ppm correspond to  $\beta$  (II) and  $\alpha$  (I) adducts (**Scheme-3.4**) in <sup>1</sup>H NMR spectra of really obtained polysilazanes (Figs. 3.3a and 3.3b).

Fig. 3.3a. <sup>1</sup>H NMR spectrum of the polymer IV (Table-1)Fig. 3.3b. <sup>1</sup>H NMR spectrum of the polymer VI (Table-1)

In case of the polyhydrosilylation reaction of dihydrosiloxanes with DAS (**Scheme-3.5**) dehydrocondensation reaction due to the interaction of NH-groups of di- and intermediate oligosilazanes with Si-H groups of dihydrosiloxanes might also proceed along with the main processes, obtaining trisilylated nitrogen atoms. To determine which process, dehydrocondensation or polyaddition is more probable, we have calculated basic energetic parameters of model systems. For this purpose we have selected structures pertaining to actual reaction products reported before:



**Scheme-3.5**

In spite of the fact that the formation of model systems containing the trisilylated nitrogen atom is thermodynamically possible ( $\Delta H_{\text{form}}^{\text{III}} = -929$  kJ), we have found earlier<sup>35</sup> that formation of hydrogen does not occur. At the same time, IR spectra of products of this reaction do not show absorption for trisilylated nitrogen atoms ( $960\text{-}950\text{ cm}^{-1}$ )<sup>54,55</sup>.

Evidently, it is favourable for dihydrosiloxanes to attract terminal allyl groups rather than NH-groups bonded to silicon atoms, surrounded with organic radicals under the conditions of polyhydrosilylation reactions. That leads to the formation of macromolecules with linear structure (**Scheme-3.1**)<sup>55</sup>.

To evaluate the structures of the products, we have performed Wade Engle X-ray diffractometry. Several diffratograms are displayed in Fig. 3.4 and show that the products are amorphous substances.

Differential scanning calorimetry (DSC) on these products have been performed. The DSC traces are shown in Fig. 3.5. Only glass transition T peaks are seen; no melting confirms the X-ray results. There is no crystallinity in these products.

Further, we have evaluated the thermal stability of products by thermogravimetric analysis (TGA) and differential thermal analysis. The thermal stability of these polymers exceeds that of polydimethylcarbosiloxanes containing terminal functional groups<sup>55</sup>. This fact may be explained by formation of intermediate stable cross-linked macromolecules from reaction of N-H groups of polysilazanes with H<sub>2</sub>N-Si groups of linear oligomers<sup>55</sup> at high temperature (210-230 °C in the open air). Such oligomers may be obtained *via* hydrolysis of Si-NH-Si bonds by air moisture. Intensive thermal degradation of present polymers begins only above

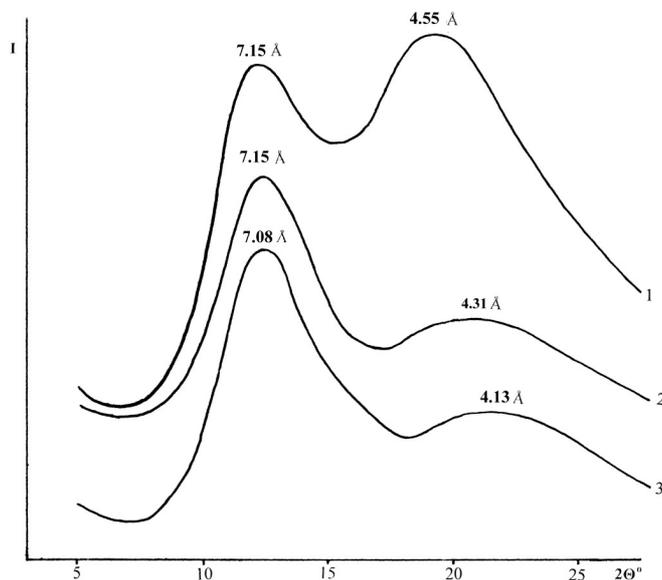


Fig. 3.4. Diffractograms of polymers: 1 = II; 2 = IV; 3 = V (Table-1)

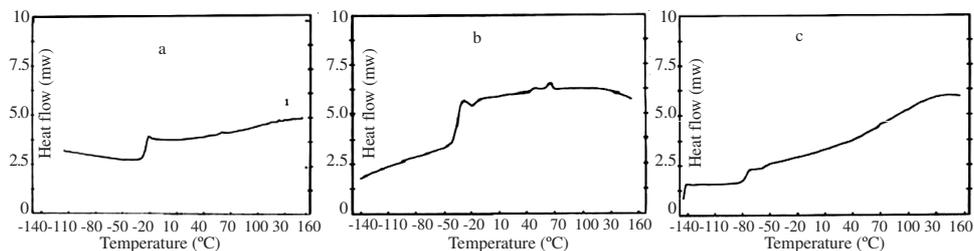


Fig. 3.5. DSC curves of polymers: II (a), VI (b), IV (c) (Table-2.14)

350 °C. Based on the obtained TGA curves the calculated  $E_a = 64$  kJ/mol exceeds the correspond parameter (52-54 kJ/mol) for polydimethylcarbosiloxanes with terminal functional groups<sup>54</sup>.

#### 4. Thermomechanical properties and thermostability of polymers containing simultaneously Si-N and Si-O groups

Thermomechanical properties and thermostability of silazasiloxyarylene polymers are reported earlier<sup>58,59</sup>.

Character of thermomechanical curves (Figs. 4.1-4.4) depends on the ratio of initial monomers, on the volume of organic radicals at silicon atoms and on the nature of aromatic diols. Under condition of permanent load acting upon polymer sample, when load increases from 30 to 100 g, area of highly elastic (elastomeric) deformation disappears on the thermomechanical curve and glazing temperature ( $T_g$ ) decreases significantly<sup>22,23</sup>.

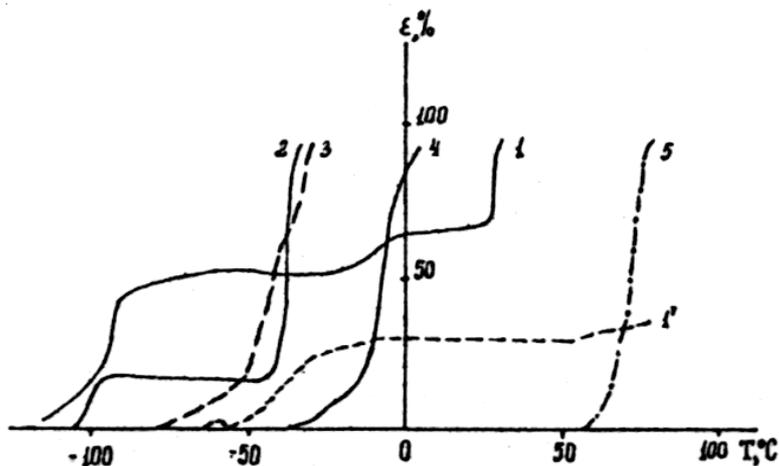
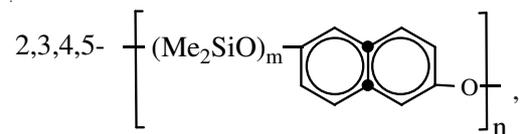


Fig. 4.1. Thermomechanical curves of the following polymers:



where: (2)  $m = 48$ , (3)  $m = 25$ , (4)  $m = 3$ , (5)  $m = 1$

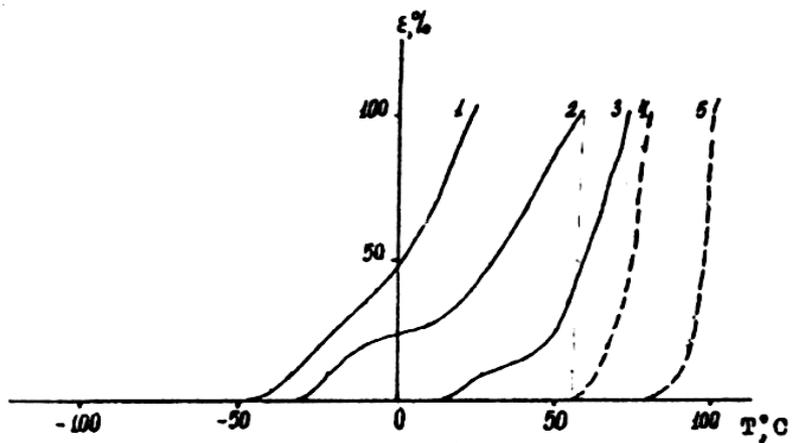
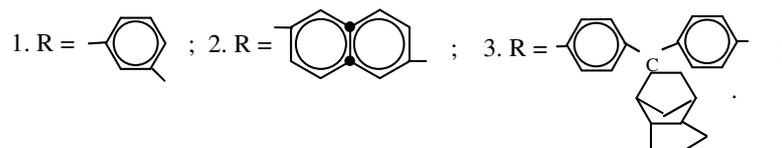
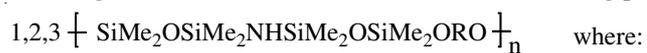


Fig. 4.2. Thermomechanical curves of the following polymers:



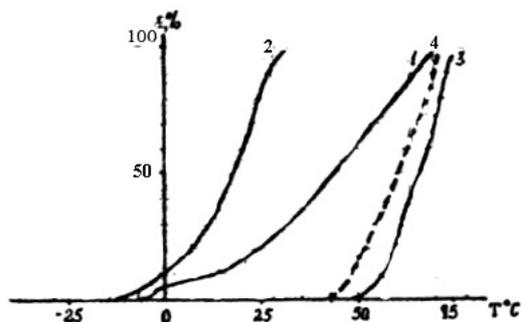


Fig. 4.3. Thermomechanical curves of the following polymers:

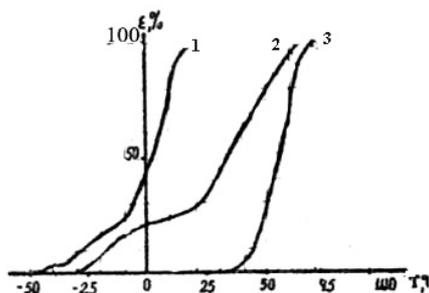
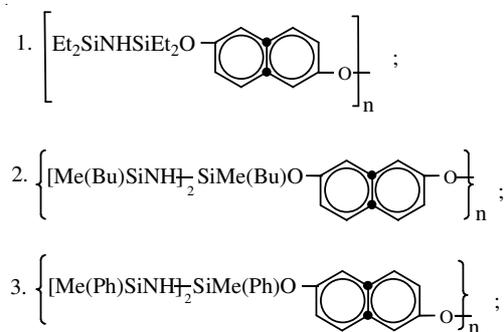
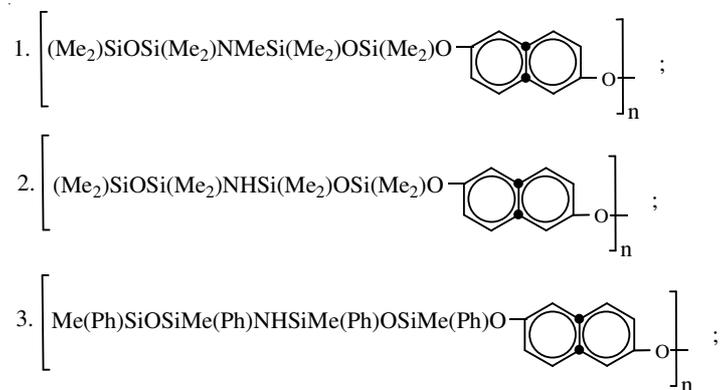
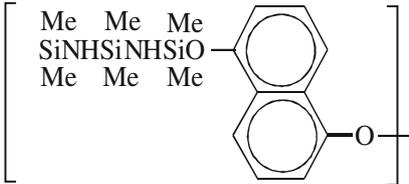
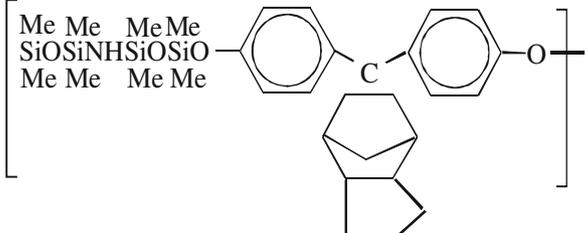
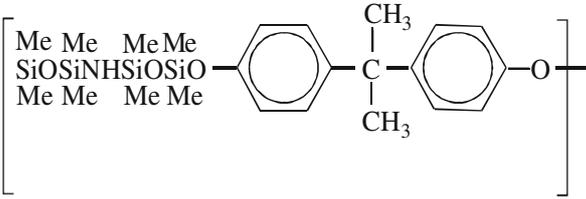


Fig. 4.4. Thermomechanical curves of the following polymers:



Area of high elasticity doesn't appear on the thermomechanical curve in case of polymers of siloxyarylene type ( $[-\text{SiR}(\text{R})-\text{O}-\text{X}-\text{O}-]$ ) and they are characterized by relatively high glazing temperature ( $T_g = 38-93\text{ }^\circ\text{C}$ ) (Figs. 4.1-4.4) in comparison with polyorganosiloxanes<sup>22,31</sup>. The high glazing temperature is distinctive for polyorganosilazasyloxyarylenes, that should be connected with comparatively strong interaction between chains (in comparison with siloxyarylenes) because of the existence of N-H bonds in the macromolecules. As expected, trimethyltriphenyl- and hexaphenylcyclotrisiloxanes form polymers with more high glazing temperature (Table-4.1), in comparison with polymers synthesized on the basis of hexamethylcyclotrisiloxanes and that is caused by content of hard phenyl radicals bonded with silicon atoms in macromolecules<sup>22,23</sup>.

TABLE-4.1  
ELEMENTAL ANALYSES OF POLYDIMETHYLSILAZASILOXIARILENS  
TILL AND AFTER DESTRUCTION

No.	Formula of elementary link of polymer	Found (%): Till destructin (after destructin)		
		C	H	N
I		52.98 (48.23)	23.24 (25.40)	2.28 (1.90)
II		60.43 (55.05)	17.77 (20.19)	3.90 (2.86)
III		58.58 (52.83)	18.35 (20.96)	3.13 (2.54)

Polyorganosilazasyloxyarylenes containing flexible aliphatic radicals bonded with silicon atoms are characterized with most low glazing temperature among synthesized polymers and they represent viscous liquids<sup>22,31</sup>.

Studies of thermal and thermal oxidative destruction of synthesized polymers carried out by thermogravimetric, differential thermal analysis (Figs. 4.5-4.8) and

chromatographical analysis show that thermal properties of polymers are basically determined by the structure of appropriate cyclosilazane (Tables 4.1 and 4.2). Table-2.9 shows that by insertion of NH-groups and aromatic groups in the polyorgano-siloxanes macro chain temperature range of destruction shifts by 10-50 °C towards the more high temperatures, that is connected by essential change of polysiloxanes destruction mechanism<sup>58</sup>. Besides, existence of aromatic groups, as well as of branches in the polymeric macro chain has a significant impact on the run of deep stage of destruction and causes the weight increase of non-volatile part of experimental objects (Fig. 4.9).

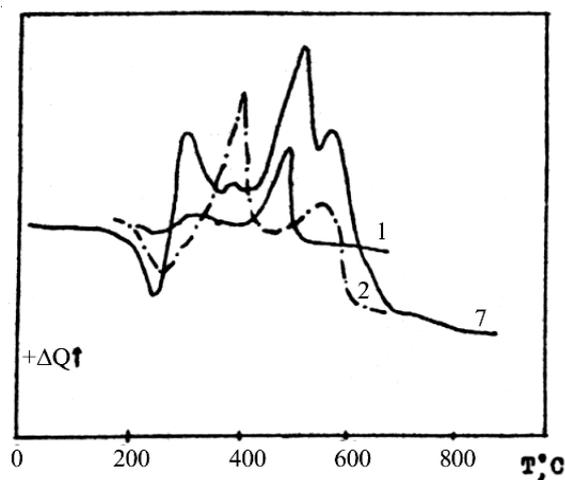


Fig. 4.5. DTA curves of the polymers I, II and VII (Table-4.2)

It is known that during high temperature destruction of siloxane polymers two competitive processes, depolymerization of basic chain and structurization of macromolecule, run and they occurs with removal or oxidation of organic groups bonded with silicon atoms (Table-4.2).

Destruction of polydimethylsiloxane (siliconorganic polymer widely used in the industry) in the inert area or in the vacuum basically runs by depolymerization mechanism, at the expense of ionic admixtures or by means of hydroxylic groups, which may be a part of polymers, or else may form during the destruction process<sup>58</sup>.

It was found out that insertion of silazane and siloxyarylene groups in the siloxane chain significantly increases the thermal stability of polymethylsiloxane<sup>58</sup>. Study of polydimethylsilazasiloxiarylenes thermal destruction shows that these polymers differ by high stability and completely destruct only at 600-620 °C temperatures (in the inert gas area) (Figs. 4.5-4.7). Existence of small quantities of branched trisilylaminogroup in the macrochain does not inhibit complete destruction of polymers<sup>58</sup>.

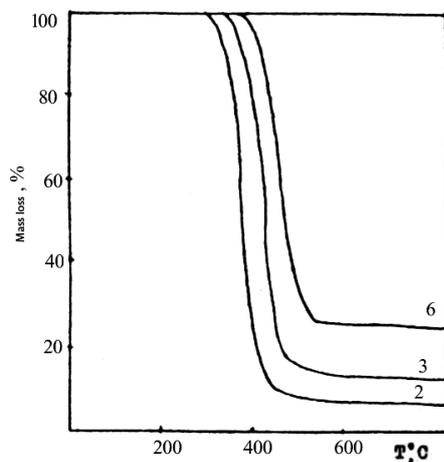


Fig. 4.6. DTA curves of the polymers II, III and VI (Table-4.2) in the air

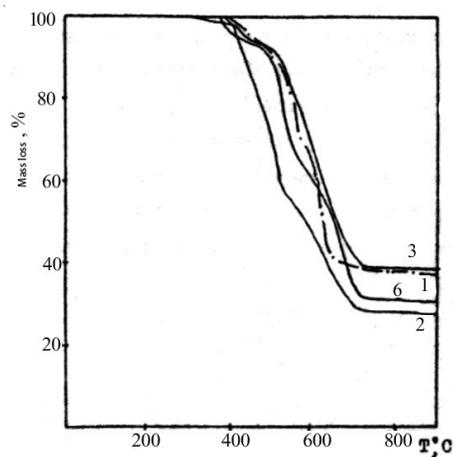
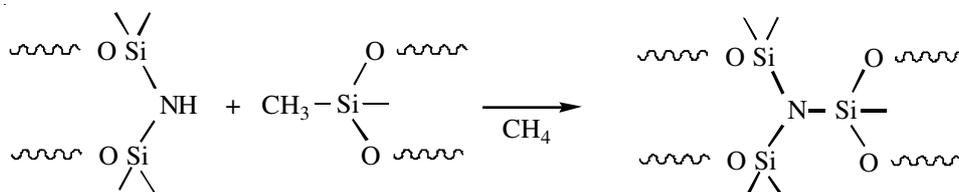


Fig. 4.7. DTA curves of the polymers I, II, III and 6 (Table-4.2) in the Helium area

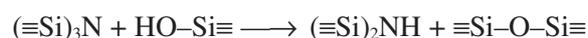
It should be noted that in case of SiNHSi-groups containing polymers II, centers of branching similar to above-mentioned may form during destruction process at the expense of the following reaction (**Scheme-4.1**)<sup>31</sup>:



**Scheme-4.1**

Thermal stability of received polymers increases in comparison with polydimethylsiloxane and that shows itself by the shift of temperature range of destruction basic process towards the higher temperatures<sup>58</sup>.

Destruction of bonds containing tertiary nitrogen atoms, existing in the polymers macro-chains or originated during destruction process possibly runs as result of current reactions between these groups and OH-groups (**Scheme-4.3**)<sup>58</sup>:



**Scheme-4.2**

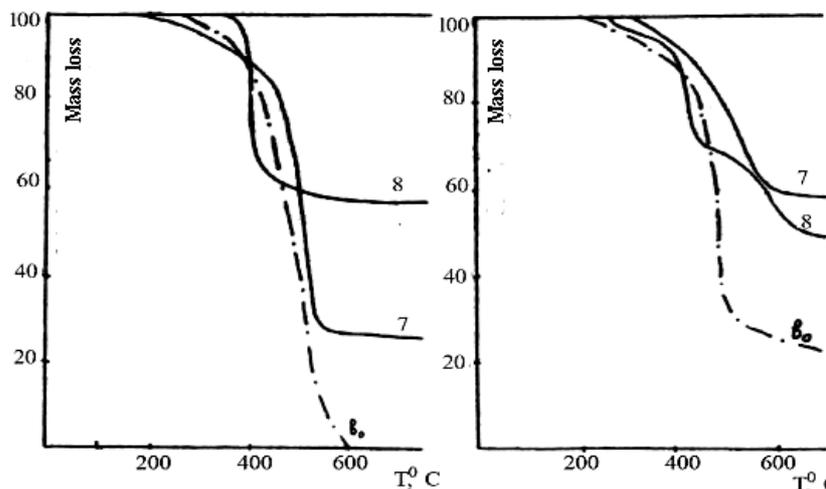


Fig. 4.8. Curves of the TGA of VII and VIII (Table-4.2) in the air

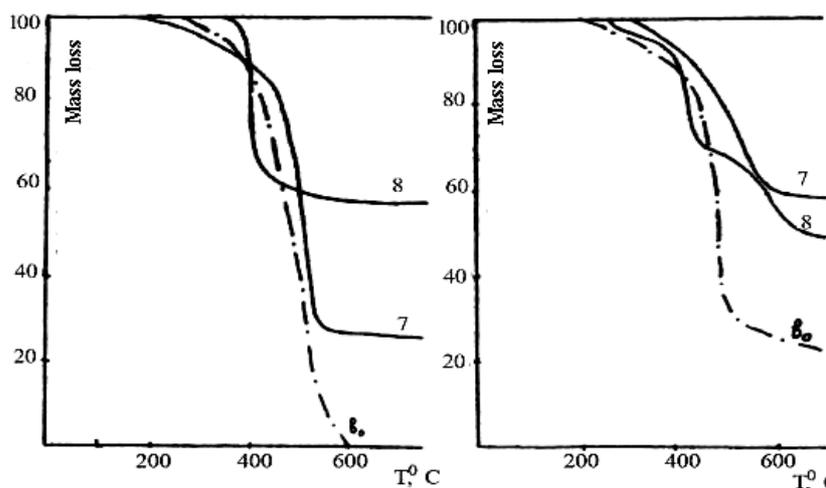
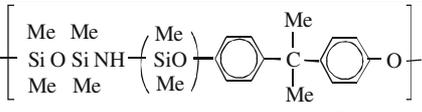
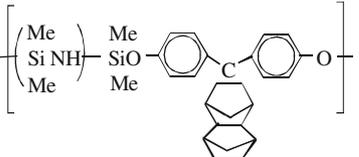


Fig. 4.9. Curves of the VII and VIII (Table-4.2) in the helium

Influence of  $(\equiv\text{Si})_2\text{NH}$  and  $(\equiv\text{Si})_3\text{NH}$  groups on the thermal and thermal-oxidative stability of polyorganosilazasyloxyarylenes is studied. It is noted that the content in the polyorganosilazasyloxyarylenes macrochain is much more than in the polyorganosilazasyloxyarylenes synthesized by the method of combined polymerizational polycondensation (with plenty of diols)<sup>58</sup>. It was established by thermogravimetric analysis that the initial temperature range of thermo destruction process is to 400-480 °C for II polymer (Table-4.2), while range of thermal-oxidative destruction is 310-440 °C; for III polymer, it is 340-410 °C, in the inert gas area and 290-410 °C in the air, respectively<sup>58</sup>. Destruction process for both polymers runs with more intensity in the 470-520 °C temperature range and is characterized by high

TABLE-4.2  
DATA OF THERMAL AND THERMOOXIDATIVE DESTRUCTION OF  
POLIORGANOSILAZASILOXANES AND SILAZASILSESQVIOXANES

No.	Elementary link of polymer	A	B	C	D	E	F
I	$\left[ \begin{array}{c} \text{Me} \quad \text{Me} \quad \text{Me} \\   \quad   \quad   \\ \text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{NH} \text{---} (\text{SiO}) \\   \quad   \quad   \\ \text{Me} \quad \text{Me} \quad \text{Me} \end{array} \right]_{17}$	He	280	380	500	100	–
		Air	220	380	490	85	–
II	$\left[ \begin{array}{c} \text{Me} \quad \text{Et} \quad \text{Me} \quad \text{Et} \\   \quad   \quad   \quad   \\ \text{---} \text{Si} \text{---} \text{NH} \text{---} \text{Si} \\   \quad   \quad   \quad   \\ \text{---} \text{Si} \text{---} \text{NH} \text{---} \text{Si} \text{---} \text{Si} \text{---} \text{Et} \\   \quad   \quad   \quad   \\ \text{Me} \quad \text{Et} \quad \text{Et} \quad \text{N} \\   \quad   \quad   \\ \text{---} \text{SiO} \text{---} (\text{SiO}) \\   \quad   \quad   \\ \text{Me} \quad \text{Et} \quad \text{Me} \end{array} \right]_{10}$	He	400	475	530	75	238.4
		Air	310	440	–	42	60.2
III	$\left[ \begin{array}{c} \text{Hex} \quad \text{Hex} \quad \text{Hex} \quad \text{Ph} \quad \text{Ph} \\   \quad   \quad   \quad   \quad   \\ \text{---} \text{Si} \text{---} \text{NH} \text{---} \text{Si} \text{---} \text{NH} \text{---} \text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{O} \\   \quad   \quad   \quad   \quad   \\ \text{NH} \quad \text{NH} \quad \text{NH} \quad \text{O} \quad \text{O} \\   \quad   \quad   \quad   \quad   \\ \text{---} \text{Si} \text{---} \text{NH} \text{---} \text{Si} \text{---} \text{NH} \text{---} \text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{O} \\   \quad   \quad   \quad   \quad   \\ \text{Hex} \quad \text{Hex} \quad \text{Hex} \quad \text{Ph} \quad \text{Ph} \end{array} \right]$	He	340	410	–	43	69.0
		Air	290	410	670	51	25.5
IV	$\left[ \begin{array}{c} \text{Me} \\   \\ (\text{SiO}) \\   \\ \text{Me} \end{array} \right]_4 \text{---} \text{C}_{10}\text{H}_6 \text{---} \text{O}$	He	325	370	410	93	–
		Air	310	420	570	71	–
V	$\left[ \begin{array}{c} \text{Me} \quad \text{Me} \\   \quad   \\ \text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{NH} \text{---} (\text{SiO}) \\   \quad   \quad   \\ \text{Me} \quad \text{Me} \quad \text{Me} \end{array} \right]_2 \text{---} \text{C}_{10}\text{H}_6 \text{---} \text{O}$	He	360	410	475	87	24.0
		Air	330	430	580	76	15.5
VI	$\left[ \begin{array}{c} \text{Me} \quad \text{Me} \\   \quad   \\ \text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{NH} \text{---} (\text{SiO}) \\   \quad   \quad   \\ \text{Ph} \quad \text{Ph} \quad \text{Ph} \end{array} \right]_2 \text{---} \text{C}_{10}\text{H}_6 \text{---} \text{O}$	He	380	465	510	76	29.7
		Air	370	490	640	69	19.4
VII	$\left[ \begin{array}{c} \text{Me} \quad \text{Me} \\   \quad   \\ \text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{NH} \text{---} (\text{SiO}) \\   \quad   \quad   \\ \text{Me} \quad \text{Me} \quad \text{Me} \end{array} \right] \text{---} \text{C}_{10}\text{H}_6 \text{---} \text{C} \text{---} \text{C}_{10}\text{H}_6 \text{---} \text{O}$	He	390	450	500	74	30.0
		Air	360	470	630	61	–
VIII	$\left[ \begin{array}{c} \text{Me} \\   \\ (\text{SiNH}) \\   \\ \text{Me} \end{array} \right] \text{---} \text{SiO} \text{---} \text{C}_{10}\text{H}_6 \text{---} \text{O}$	He	260	500	625	84	–
		Air	390	510	610	63	22.6
IX	$\left[ \begin{array}{c} \text{Me} \\   \\ (\text{SiNH}) \\   \\ \text{Me} \end{array} \right] \text{---} \text{SiO} \text{---} \text{C}_{10}\text{H}_6 \text{---} \text{O}$	He	280	475	560	84	–

X		He	370	425	480	88	23.4
		Air	260	365	580	64	–
XI		He	350	400	490	74	–

A = The medium; B = Temperature of the beginning of destruction (°C); C = Temperature of destruction on 10 % (°C); D = Temperature of destruction on 50 % (°C); E = Loss of the mass (%); F =  $E_{\text{effect}}$  (kJ/mol).

activation energy in the inert area. Quantity of non-volatile part of these polymers significantly increases at more high temperatures and exceeds the similar data of other polymers (Table-4.1). Weight loss is 1-2 % in the temperature range 140-300 °C. This fact is probably connected with functional groups participation in the current condensation process, which is followed by separation of volatile accompanied products. Initial temperature of destruction of polymers containing arylene groups depends on the content of NH-group in the elementary ring. For example, in case of VIII and IX polymers (Table-4.2), which contain two NH-groups in the elementary ring weight loss begins at 260-280 °C under destruction conditions, at the same time, for IV, V, VI, VII and X polymers (Table-4.2), which don't contain any NH-groups in the macromolecules elementary rings or else contain only one NH-group, initial temperature range of weight loss is 325-390 °C<sup>58</sup>.

Endothermal and exothermal effects are revealed on the thermograms of II and VIII polymers (Fig. 4.5), which probably are connected with post-condensation processes in the functional groups and with separation of volatile products or else (in case of II polymer) with ring expansion at the expense of possible rearrangement reaction<sup>38</sup>. By the increase of temperature exothermal effect with clearly defined peaks at 490, 530 and 580 °C becomes apparent and it corresponds with basic process of polymer destruction. As to polyorganosilazasyloxyarylenes destruction, its basic exothermal effect is revealed at 375 and 465 °C temperatures and that proves that shift of basic exothermal effect towards high temperatures takes place (in comparison with polydimethylsiloxanes) due to insertion of  $(\equiv\text{Si})_3\text{N}$ ,  $(\equiv\text{Si})_2\text{NH}$  groups or simultaneous insertion of aromatic and NH-groups in the siloxane chain<sup>22,58</sup>. It is a clear evidence of the stabilizing effect of above-mentioned groups during destruction processes.

More strong stabilizing effect of NH-groups is revealed in case of polymers, elementary rings of which contain two or more such groups. According to TGA data mass loss, both in inert gas area and in the air is equal to 20-25 % in the temperature range 300-400 and 300-500 °C, respectively<sup>22</sup>. Proceeding from the data calculated according methyl groups content in the elementary ring of IV, V, VII and X polymers (Table-4.2) we can assume that in the given temperature range

polymer structurization process simultaneously runs along with removal of this group<sup>58</sup>.

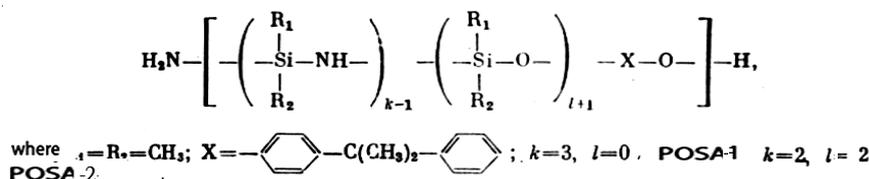
For the confirmation of above mentioned idea thermodestruction process of VII, VIII and X polymers was studied (in the air,  $T = 400^{\circ}\text{C}$ ) (Tables 4.1 and 4.2)<sup>58</sup>. Change of C/Si ratio before destruction and after it was selected as a criterion of estimation of oxygenized or separated methyl groups. As it seen from Table-2.9, C/Si ratio significantly changes and that proves the separation of methyl group located near silicon atom. Study of thermal destruction of IV and V polymers (Table-2.10) in the air, at  $450^{\circ}\text{C}$  (along with analysis of gas products) allows us to prove above mentioned idea, since methane and hydrogen were the main gas products of thermal destruction. Decrease of intensity of corresponding absorption bands ( $815\text{-}805$ ,  $1270\text{-}1260$  and  $2965\text{-}2910\text{ cm}^{-1}$ ) of methyl and C-H group after destruction, under testing condition are revealed in the infrared spectrum of the same polymers samples, while absorption bands ( $960\text{-}950\text{ cm}^{-1}$ ) more characteristic for  $(\equiv\text{SiN})_3\text{N}$  groups become more intensive<sup>58</sup>. Thus, for all studied polymers the separations of organic groups from silicon atoms of main chain and structurization of macrochain are the main processes in the given temperature range. Above  $500\text{-}550^{\circ}\text{C}$  temperatures, destruction process takes place, which completes with intensive destruction (desintegration) of basic chain of macromolecules. The rate of polymer desintegration and weight of solid residue significantly depends on the content of SiNHSi-group in the elementary ring of polyorganosilazasyloxyarylene and on the destruction conditions (Table-4.2; Figs. 4.5-4.7)<sup>58</sup>.

The investigation of the thermooxidative destruction (TGA, DTA) of the polysilazasiloxiarylenes showed that their thermo-oxidative stability is higher than the organo-silicon polymers<sup>58</sup> (Figs. 4.6-4.8). As it is seen, the lowest weight losses are observed for polymers based on trimethyltriphenylcyclotrisiloxane with heteroarylene bisphenols (1:1). The last fact can be explained not only by the stabilizing effect of the electron-acceptor phenyl groups influence on the SiNHSi and SiOC<sub>cp</sub> bonds but also by the cross linking reaction of the polysilazane chains caused by subtracting the phenyl-groups from Si and forming the intermediate cross-linked structures at extension. This leads to enhancing of the thermo-oxidative destruction temperature. This assumption is confirmed by the DTA data. Thus, in the temperature interval  $340\text{-}350^{\circ}\text{C}$ , there is an exothermic peak corresponding to the subtraction of the phenyl groups (the mass loss is less than 20-25 %)<sup>34,58</sup>.

##### **5. Modification of properties of resin compositions and vulcanizates prepared on the basis of all-hydrocarbon elastomers by polyorganosilazasyloxyarylenes**

Use of various organic and organoelemental compounds for modification of properties of resin compositions and appropriate vulcanizates, prepared on the basis of carbonchain rubber resin (caoutchouc) is described in the literature<sup>59-63</sup>.

Lekishvili *et al.*<sup>64</sup> used polyorganosilazasyloxyarylenes (POSA) as modifiers of above mentioned systems, which were obtained by them in the mass, by interacting organic cyclic silazane with bisphenol-A.



Scheme-5.1

It is known that amino compounds have a specific impact on the character of structural modifications of elastomers at high temperatures. Study of impact of small additions of POSA on the chemorheological properties of resin composites and on the physical and mechanical characteristics of appropriate vulcanizates has become the subject of special interest.

TABLE-5.1  
 CHEMORHEOLOGICAL PROPERTIES OF THE ELASTOMERS WITH 0.5 WEIGHT RATIO (NUMERATOR) OR 1.5 WEIGHT RATIO (DENOMINATOR) POSA

Composition	$\eta_{\text{sv}}$ in conventional unites	$\tau$ (min)	$\Delta\tau$ (min)	n, when $\dot{\gamma} = \text{const}$ , $\text{MПа}\cdot\text{c}$	K, $\text{kПа}\cdot\text{c}$	n, when $\dot{\gamma} = 05 \text{ c}^{-1}$ , $\text{MПа}\cdot\text{c}$	n
Without addition	43	18	7	83	125	710	0.27
POSA-1	40/31	18/17	6/5	80/72	120/108	700/680	0.27/0.24
POSA-2	40/29	18/17.5	6/5	80/70	124/100	708/663	0.27/0.25

Resin compositions compound (m. fraction per 100 m. fraction of rubber resin) was the same: *cis*-isoprene caoutchouc SKI-3-100, sulphur-2.5, sulfonamide c-100, zinc oxide-5, diaphene "FP" (anti-ageing agent)-2.0, technical carbon "DG"-100 - 30.0, POSA-0.5 and 1.5; composition has been prepared on the roll mills, at temperature  $80 \pm 3$  °C, while vulcanization were carried out in the press arrangement, at 143 °C. Resin compositions viscosity and vulcanization properties were estimated by means of rotation viscometer at 120 °C, while shearing rate was  $\dot{\gamma} = 1.2 \text{ s}^{-1}$ . Rheological characteristics (effective viscosity and liquidity index) were determined by capillary viscometer<sup>64</sup>.

Time change of effective viscosity of samples, containing POSA (according to Moony) is shown on the fig. Table-5.1 confirms the viscosity and vulcanization (chemo-rheological) changes in resin compositions during insertion of various amount of POSA. In particular, plasticizing effect of additions in the wide range of shearing rate takes place. Insertion of POSA also has an influence on the character of composition liquidity, strengthens appearance of non-Newton properties<sup>64</sup>. Thus, similar to previously described silicon-organic compounds<sup>64</sup>, POSA is characterized by molecular plasticization. As it seen from Table-5.1, POSA accelerates vulcanization processes in resin compositions, which is associated with existence of active Si-NH<sub>2</sub>-groups in its molecule<sup>64</sup>, intermediate concentration of which may increase at the expense of hydrolysis of SI-NH-bonds of polyorgano-silazasiloxiarylenes by air damp.

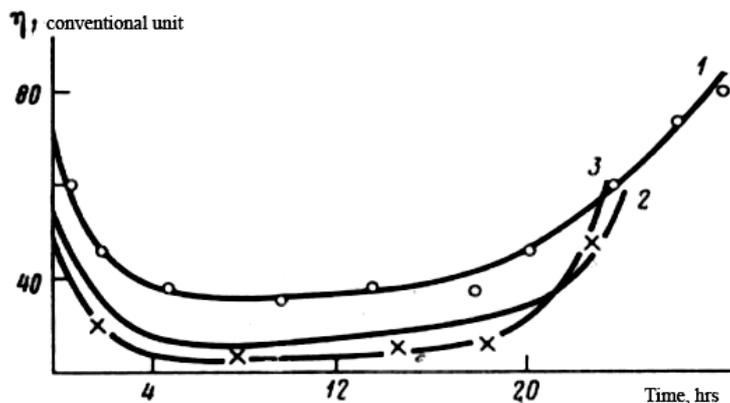


Fig. 5.1. Change of viscosity of the rubber compositions (by Moony) in the time: (1) Without the modifier agent; (2) & (3) In presence of 1.5 weight ratio of POSA-1 and POSA-2, correspondingly

TABLE-5.2  
PHYSICAL, MECHANICAL AND DYNAMIC PROPERTIES OF ELASTOMERIC  
COMPOSITION, CONTAINED 0.5 WEIGHT RATIO (NUMERATOR) OR  
1.5 WEIGHT RATIO OF THE POSA (DENOMINATOR)

Composition	A	B	C	D	E	F
Without addition	2.15	23.0	760	54	0.90	87.00
POSA-1	2.25/2.30	28.2/25.6	750/810	53/52	0.86/0.82	126/274
POSA-2	2.20/2.25	28.9/26.8	830/780	50/51	0.87/0.81	120/230

A = Mod. at the 200 %-elongation, MPa; B = Conventional strength at the elongation, MPa; C = Relative strength at the break (%); D = Hardness by SHORI, conventional units; E = Coefficient of the thermal aging (80°, 48 h); F = The endurance at the multiple deformation (70°, 20/100 %), thousand cycles.

Results given in Table-5.2 confirm that insertion of small additions of POSA in the above-mentioned resin compositions significantly improves the complex of physical, mechanical and dynamic properties, which are distinctive for them<sup>64</sup>.

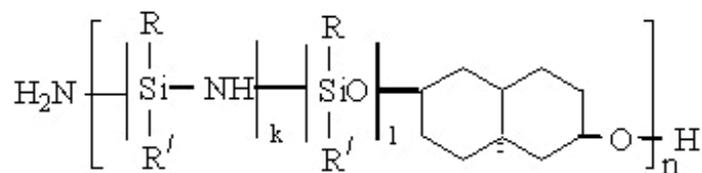
There are weak absorption bands of vulcanized compositions in the IR spectrum (in 830, 950-947 and 1080-1060  $\text{cm}^{-1}$  ranges), which are distinctive for Si-CH<sub>3</sub>, Si-NH-Si and Si-O-Si bonds, respectively<sup>64</sup>. On the basis of these data it was determined that during vulcanization process POSA interacts chemically with unsaturated molecules of SCI-3. It is possible to suppose, that polar macromolecular fragments generated at this time increase the total level of physical interactions in the vulcanization network. As a result, additional weak bonds are arisen. Such bonds fission much faster during deformation than cross bonds (atomic bridges) or chemical bonds of rubber basic chain, which causes reduction of local tensions and lowering of elastomers' macrochains orientation toward direction of deformation. Thus, it is possible to consider POSA as modifier of polyfunctional action of resin compositions and their vulcanized products.

## 6. Physical and chemical modification of oligomethylsiloxanes by polyorganosilaza siloxyarylenes in the treatment process

Oligomethylsiloxane with divergent structure (OMS) has a wide application as press-materials binding oligomer<sup>65</sup>. Its solidification process is long standing, runs at high temperatures and needs additional heat treatment. At the same time, products prepared on its basis often don't meet the requirements which are imposed to them under service conditions<sup>66</sup>.

There are literary data about solidification of oligomethylsiloxane by various polyorganosiloxanes<sup>66</sup>, which accelerate this process, but don't improve their physical and mechanical properties. These studies are basically carried out towards the OMS treatment and therefore, attention is paid to the regulation of structure and to the properties of obtained materials.

By taking into consideration the peculiarities of OMS chemical structure (existence of tension cycling fragments and marginal hydroxyl group), polyorganosilazasiloxiarylenes (0.1-1 mass %) were used for regulation of solidification processes and properties of branched PMS (**Scheme-6.1**)<sup>22</sup>.



where  $k = 0 \div 3$ ,  $l = 0 \div 3$

$k + l = 3; 4$ .

**Scheme-6.1**

The depth of structurization in the presence of polyorganosilazasiloxiarylenes was determined by various methods, which was caused by difficulty of solidification quality control<sup>22</sup>.

As it seen from extraction data (Fig. 6.1) OMS solidification quality depends on the temperature of solidification and chemical structure of polyorganosilazasiloxiarylenes added to it<sup>22</sup>. Structurization process runs more completely in polyorganosilazasiloxiarylenes case, silicon atoms of which are bonded with methyl groups of small size. Because of it, process of space structure formation accelerates significantly<sup>66</sup>.

Thermomechanical study data give us a complete idea of the density of space (three-dimensional) network, formed during OMS solidification. As it seen from Fig. 6.2, insertion of polyorganosilazasiloxiarylenes in OMS composition decreases sample deformation and raises glazing temperature in comparison with initial PMS<sup>66</sup>.

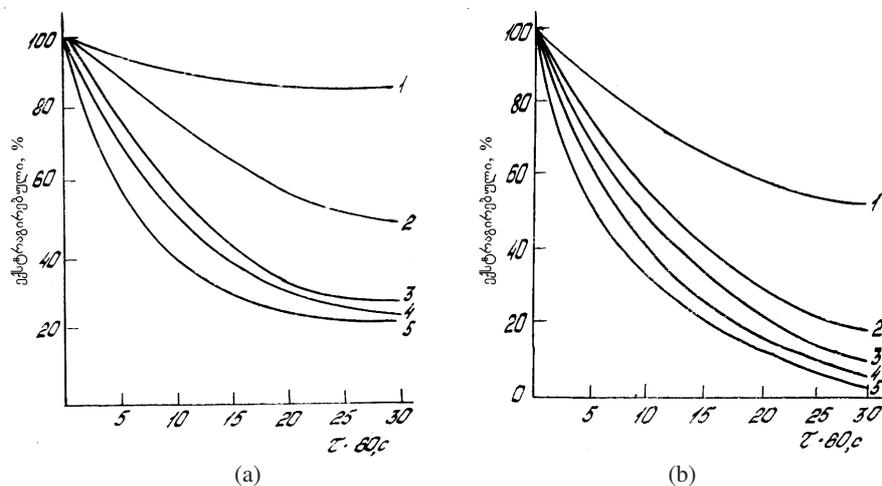


Fig. 6.1a,b. The dependence of the extracted compounds mass on the the composition hardening time  $T = 423$  K (a) and  $T = 443$  K (b) for non-modified OMS (1) and OMS modified by polyorganosilaxasiloxiarylenes (1 %): (2)  $R = R' = C_6H_5$ ; (3)  $R = R' = C_4H_9$ ; (4)  $R = R' = C_2H_5$ ; (5)  $R = R' = CH_3$

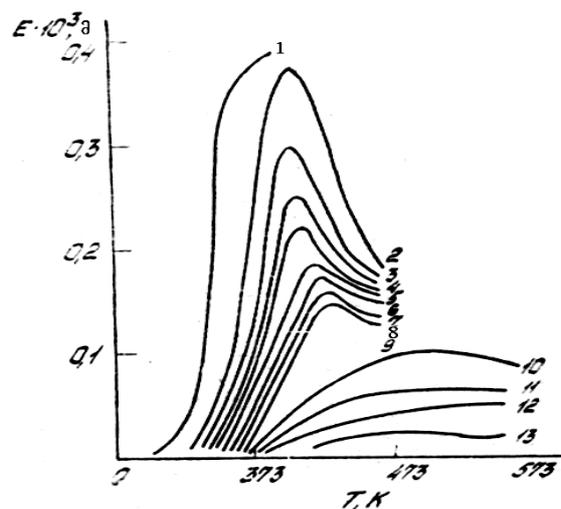


Fig. 6.2. Thermomechanical curves for non-modified OMS (1) and OMS modified by polyorganosilaxasiloxiarylenes (2-13); (2) 0.1 %; (3) 0.1 %; (4) 0.1 %; (5) 0.1 %; (6) 0.05 %; (7) 0.5 %; (8) 0.5 %; (9) 0.5 %; (10) 1. %  $C_6H_5$ ; (11) 1 %  $C_4H_9$ ; (12) 1 %  $C_2H_5$ ; (13) 1 %  $CH_3$

The present studies show, that increase of solidified OMS space network density takes place in the presence of silazane modifiers, which is confirmed by determination of deformation heat stability according to Wick<sup>65,66</sup>. Deformation heat stability increases along with increase of amount of added polyorganosilaxasiloxiarylenes and it is

determined by nature of organic radicals bonded with silicon atoms in the addition. It was also confirmed that heat resistance of polymer-compositions reduces by increase of volume of organic groups bonded with silicon atoms in the modifier agent (Table-6.1)<sup>66</sup>. Temperature range, in which the process of OMS structurization runs intensively, was determined by thermographic studies. As it seen from experimental data, structurization temperature is basically depended on the quantity and chemical nature of modifiers (Fig. 6.2).

The process of product formation is especially important, along with necessary completion of chemical reaction of network polymer formation during the treatment of plastic materials prepared on the basis of received silicoorganic compounds. Whole complex of physical and chemical properties of received materials and their stability during product's operational process depend on the quality of completion of the structurization reaction (FigS. 6.3 and 6.4). Completion of solidification reactions and rate of their performing, in its turn, is determined by reaction capability of the substrate and by chemical nature of polyfunctional modifier agent<sup>66</sup>.

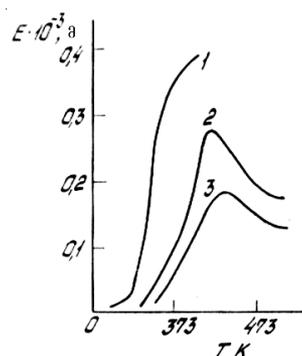


Fig. 6.3. Thermomechanical curves of non-modified OMS (1) and OMS modified by polyorganosilazasiloxarylilene additives (2.  $R = R' = C_2H_5$ ; 3.  $R = R' = C_6H_5$ )

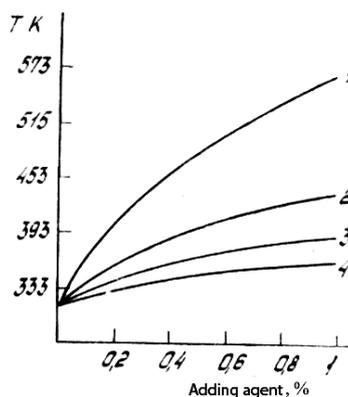
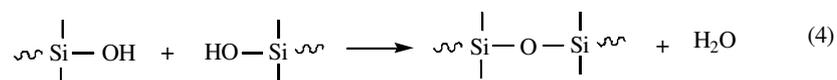
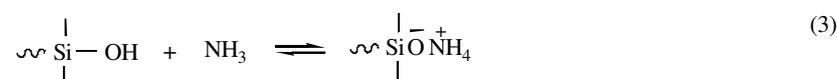
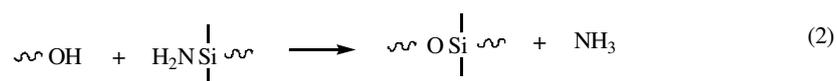
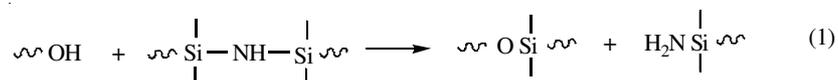


Fig. 6.4. Dependence of the heatresistance of the OMS on the amount of polyorganosilazasiloxarylilene additives (**Scheme-7.1**): (1)  $R = R' = C_6H_5$ ; (2)  $R = R' = C_4H_9$ ; (3)  $R = R' = C_2H_5$ ; (4)  $R = R' = CH_3^U$

Researches carried out for determination of polyorganosilazasiloxiarilenes impact on the OMS structurization and properties of received composites show that process of OMS structurization significantly accelerates at their presence, that is connected by their interaction with SiNHSi-groups of silanols group modifier (**Scheme-6.2**)<sup>23</sup>. In the authors opinion, nucleophilic particle  $\equiv\text{Si}-\text{ONH}_4$  formed by interaction with ammonia excreted by  $\equiv\text{Si}-\text{OH}$  groups accelerates the process of hydroxyl groups homocondensation, that, finally, assists formation of space network structure<sup>64</sup>. At the same time OMS solidification temperature decreases and density of space network created as a result of solidification increases that are connected by the alloying effect, caused by insertion of small amount of additions, their placement on the surface of structure elements and formation of polymer systems with high dynamic properties<sup>46</sup>.



Scheme-6.2

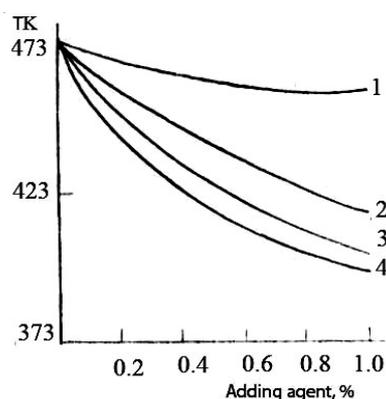


Fig. 6.5. Dependence of the temperature of the structurization on the amount of polyorganosilazasiloxiarilene additives (**Scheme-7.1**): (1)  $\text{R} = \text{R}' = \text{CH}_3$ ; (2)  $\text{R} = \text{R}' = \text{C}_2\text{H}_5$ ; (3)  $\text{R} = \text{R}' = \text{C}_4\text{H}_9$ ; (4)  $\text{R} = \text{R}' = \text{C}_6\text{H}_5$

TABLE-6.1  
MODIFICATION OF THE OLIGIMETHYLSILOXANE BY  
POLYORGANOSILAZASILOXYARILENES

No.	Composition	A	B	C	D
1	(OMS) $[\text{CH}_3\text{SiO}_{1.5}]_n$	38	180	477	250
2	OMS* + 0.5% $\left[ \text{Si}(\text{CH}_3)_2\text{NH}_2\text{Si}(\text{CH}_3)_2\text{O} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \\ \text{---} \text{C}_6\text{H}_4 \text{---} \end{array} \right]_n$	86	240	880	–
3	OMS + 2.0% $\left[ \text{Si}(\text{CH}_3)_2\text{NH}_2\text{Si}(\text{CH}_3)_2\text{O} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \\ \text{---} \text{C}_6\text{H}_4 \text{---} \end{array} \right]_n$	93	340	950	60
4	OMS + 2.0% $\left[ \text{CH}_3\text{SiC}_6\text{H}_5\text{NH}_2\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \\ \text{---} \text{C}_6\text{H}_4 \text{---} \end{array} \right]_n$	84	330	860	72
5	OMS + 2.0% $\left[ (\text{CH}_3)\text{Si}(\text{C}_4\text{H}_9)\text{NH}_2\text{Si}(\text{CH}_3)(\text{C}_4\text{H}_9)\text{O} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \\ \text{---} \text{C}_6\text{H}_4 \text{---} \end{array} \right]_n$	88	320	1050	54
6	OMS + 2.0% $\left[ \text{Si}(\text{CH}_3)_2\text{NH}_2\text{Si}(\text{CH}_3)_2\text{O} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \\ \text{---} \text{C}_6\text{H}_4 \text{---} \end{array} \right]_n$	82	280	915	40

A = Hardening degree (%); B = Deformation thermal stability (5 kG/cm<sup>2</sup>); C = Compression strength (kG/cm<sup>2</sup>); D = Strength (kG/cm<sup>2</sup>); \*OMS = Oligomethylsiloxane.

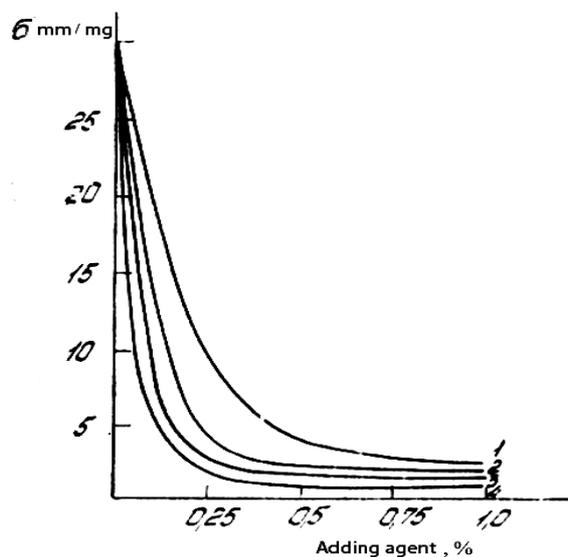


Fig. 6.6. Dependence of value of residual tension for non-modified OMS (1) and OMS modified by polyorganosilazasiloxiarylenes on their amount and the structure of the radicals at silicon atoms: (1) R = R' = CH<sub>3</sub>; (2) R = R' = C<sub>2</sub>H<sub>5</sub>; (3) R = R' = C<sub>4</sub>H<sub>9</sub>; (4) R = R' = C<sub>6</sub>H<sub>5</sub>

## 7. Modification of Polycarbonate by polyorganosilazasiloxiarylenes

Polycarbonates (macrolon, diphlon and others) are characterized by high physical and chemical properties and are widely used for preparation of constructional products. Treatment of polycarbonates by high efficiency method is complicated by necessity of high viscosity of their melts, as well as by necessity of maintenance of high temperatures during its treatment in the narrow temperature range.

In the products, manufactured from polycarbonates, it is indicated a high level of residual internal stresses, as a rule, which is caused by chain rigidity and low rate of relaxation processes. This fact causes cracking of products manufactured from polycarbonate in the treatment process and because of it their use is limited<sup>67</sup>.

Well known polycarbonate-siloxane elastomers represent polycarbonates copolymers with polyorganoiloxanes<sup>67</sup>. Main defect of such elastomers is their low heat stability and very low mechanical solidity, in comparison with common polycarbonates.

Polymeric composition manufactured on the basis of polycarbonates contains aromatic polycarbonates and polyorganosiloxanes with various viscosities - polydimethyl-siloxane and polymethylphenylsiloxane<sup>67</sup>. Polycarbonate dissolved in methylene chloride is added to liquid organosiloxanes. Films (webs) are taken from the formed solution. Compositions received by this method are characterized by low liquidity, while during their exploitation at high temperatures their mechanical solidity reduces. For the purposes of increase of above-mentioned compositions liquidity and their mechanical solidity polyorganosilazasiloxiarylenes are used as modifiers instead of polyorganosiloxanes and molecular mass of the first ones may vary from 100 thousand to 200 thousand<sup>67</sup>. Polyorganosilazasiloxiarylenes (0.1-3.0 m.n.) used for the same purposes<sup>67</sup> are capable to penetrate not-reversibly into disordered areas of polycarbonates supramolecular structure, don't initiate their swelling or opening and increase shear capacity of structural units. This fact provides acceleration of relaxation processes and lowers the level of residual stress in the product<sup>67</sup>.

It is established, that insertion of alloying doesn't require any special accommodating as well as no complication in technology of polycarbonates and allows to improve polymers treatment capacity, reduces treatment temperature by 30-60 °C. Polycarbonates (PC), obtained on the basis of diphenylolpropane and phosgene (which are manufactured with molecular mass from 25000 to 45000) are used for receiving of given composition. Well known antioxidants-tri-*p*-nonylphenylphosphates and other polyphosphates, *e.g.* polythiodiphenylenphenyl-phosphinates or stilbenes are used as stabilizers<sup>67</sup>.

As it seen from Table-3, insertion of certain amount of polyorganosilazasiloxiarylenes as alloying additions in polycarbonate increases its liquidity 2-7 times, at the same time, limit value of solidity during tension and given limit value of extension coefficient during bruise are maintained for a long period of time, in the ageing process at 120 °C, while non-modified polycarbonates have no such capacity.

TABLE-7.1  
 PROPERTIES OF THE MODIFIED POLYCARBONATE BASED ON BISPHENOL-A

Composition	Melting index, $I_{melt}$	Change of strength characteristics during of ageing ( $\sigma$ kG/cm <sup>2</sup> /ε)				$\rho$ , 10 <sup>6</sup> Hz	tgδ, 10 <sup>6</sup> Hz	E, kV mm
		Before ageing	After 5 days	After 10 days	After 30 days			
Polycarbonate (PC)	1	605/80	635/70	630/50	535/30	$3.1 \times 10^{16}$	0.0080	23.5
PC + 5 % Fluoroplast	2	567/91	580/85	555/71	515/50	$4.5 \times 10^{16}$	0.0092	21.2
PC + 1 % [Me <sub>2</sub> SiOMe <sub>2</sub> SiNHSiMe <sub>2</sub> OSiMe <sub>2</sub> ORO] <sub>n</sub>	8	631/93	646/93	640/95	630/80	$4.4 \times 10^{16}$	0.0076	24.0
PC + 1 % [MeEtSiNHMeEtSiOR'O] <sub>n</sub>	3	620/100	602/95	612/86	560/81	–	–	–
PC + 1 % [Me <sub>2</sub> SiOMe <sub>2</sub> SiORO] <sub>n</sub>	8	628/99	639/88	636/62	626/60	$2.2 \times 10^{16}$	0.0078	23.0
PC + 1 % [Me <sub>2</sub> SiOMe <sub>2</sub> SiOR'O] <sub>n</sub>	2	600/102	610/88	606/80	602/78	$2.4 \times 10^{16}$	0.0072	23.3
PC + 1 % [Me <sub>2</sub> SiO] <sub>48</sub> R'O] <sub>n</sub>	4	560/72	603/70	602/66	560/52	$4.1 \times 10^{16}$	0.0095	22.5
PC + 1 % [MeButSiNHMeButSiOR'O] <sub>n</sub>	3	665/93	650/90	648/80	632/80	$2.3 \times 10^{16}$	0.0090	21.0

TABLE-8.1  
 SOME PHYSICAL AND MECHANICAL PROPERTIES OF THE MODIFIED PHENOL FORMALDEHYDE RESIN COMPOSITE

No.*	Electrical conductivity, ρ (om cm)	Strength on pressure, σ (MPa)	Strength on winding, σ (MPa)	Specific percussive viscosity (kg cm/cm <sup>2</sup> )
I	53.28	21.22	19.80	2.76
II-1 %	49.23	21.22	12.00	2.40
III-1 %	49.63	27.16	18.50	2.45
III-3 %	49.50	56.59	16.90	2.27
IV-3 %	51.67	41.58	26.20	2.75

\*I = without modifiers (**Scheme-1**);

II = Diallylsiloxane based on 4-allyl-2-methoxyphenol:hexamethylcyclotrisiloxane (2:1);

III = Diallylsiloxane based on 4-allyl-2-methoxyphenol:trimethyltriphenylcyclotrisiloxane (2:1);

IV = Diallylsiloxane based on 4-allyl-2-methoxyphenol:hexamethylcyclotetrasiloxane (2:1).

It is established by the present studies that index of polycarbonates melting ( $I_{\text{melt}}$ ) rises with increase of alloying addition content in the composition. At the same time its solidity characteristics worsen<sup>67</sup>. Polycarbonate modification with above-mentioned alloying additions allows manufacturing such polymeric compositions, good technological properties of which are combined with increased indices of solidity. A composition prepared by this method has the wide use for producing of reinforcing constructions, electric and radio-technical details and others<sup>67</sup>. Manufacturing of above-mentioned details from pure polycarbonate is complicated because of high viscosity of its melts and, respectively, because of low liquidity, that fact necessitates increase of melt's temperature. In this case, as a rule, cracking of products manufactured from polycarbonates, as well as polymers destruction and high level of residual stress are mentioned. Polycarbonates treatment capacity improves, its liquidity increases and treatment temperature lowers by 40-60 °C<sup>67</sup> by insertion of silazasiloxiarylene alloying additions and that makes the application of these technology.

### **8. Possibility of modification of fenolformaldehyde resins by diallylsilazanes**

Synthesized diallylsilazanes and polymers based on them were used for modification of properties of some industrial polymer composites based on polymers with functional groups<sup>55</sup>.

It is observed that addition of 5-10 % of polyorganosilazanes to an adhesive containing vinyl dimethylacetylenylcarbinol increases thermal stability of the composite by 25-30 °C. The optical transparency of thin films of 100 mcm thickness was unaffected.

The satisfactory results were obtained by modification of properties of phenol formaldehyde resin (PFRs) composites with present diallylsilazanes. Thus, addition of diallylsilazanes (1-3 mass %) has improved some properties of hardened PFR (Table-8.1). Their important physical and mechanical properties of the composites have remained unchanged.

We have also performed some investigations of our synthesized oligomers and polymers in combination with phenol formaldehyde resin. These oligomers were successfully used as a binding component for polymer/graphite electro-conducting composites. Our ECCs can be recommended for making electrodes and for making chemical (fuel) sources of electrical energy<sup>68</sup>.

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