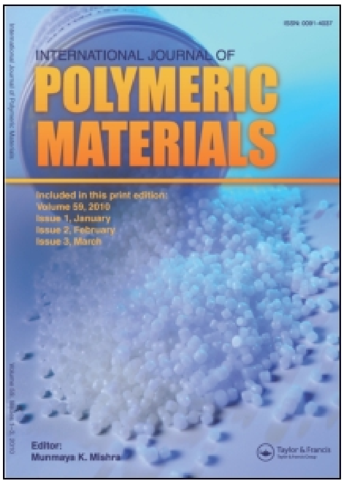

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Non-traditional Method of Synthesis of Organosilicon Polymers

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To cite this Article Khananashvili, Lotari and Lekishvili, Nodar(1997) 'Non-traditional Method of Synthesis of Organosilicon Polymers', International Journal of Polymeric Materials, 36: 3, 151 — 187
To link to this Article: DOI: 10.1080/00914039708029413
URL: http://dx.doi.org/10.1080/00914039708029413

Intern. J. Polymeric Mater., 1997, Vol. 36, pp. 151–187
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Non-traditional Method of Synthesis of Organosilicon Polymers

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The combined polymerization-condensation process-the non-traditional method of synthesis of siliconorganic polymers with organo-inorganic and inorganic main chains of macromolecules is reviewed.

Keywords: Heterocycle; combined polymerization; polycondensation; kinetic; mechanism; limiting stage; transition complex; organo-inorganic; macromolecular chain

INTRODUCTION

The traditional methods of fabrication of siliconorganic polymers (SOP) such as hydrolytic polycondensation, reaction of interchange decomposition and catalytic polymerization of heterocycles make possible to obtain the polymers with siloxane main chains of macromolecules [1]. These polymers are distinguished with many interesting properties (e.g. thermostability, hydrophobility, freeze resistance etc), but in many cases, they have low heat and irradiation resistance, low ability of adhesion and of forming the firm films. The above mentioned shortcomings of SOP can be eradicated by the introduction of different heteroatoms and spatial groups into main chain of their macromolecules by using combined polymerization-condensation (CPC) processes [2].

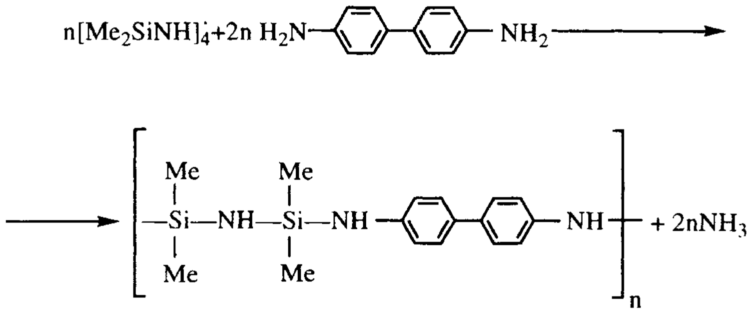
This method had found intensive development in the 80s and 90s, when there was synthesized a big variety of siliconorganic polymers with the inorganic and organo-inorganic main chains of macromolecules:

- Polyorganosiloxyarylenes, carbosiloxyarylens and -siloxysilarylenes;
- Polyorganosilazaarylenes;
- Polyorganosilazaoxyarylenes and -silazasiloxyarylenes;
- Polyorganosilazasiloxyheteroarylenes;
- Polyorganosilazasiloxycarbonates and -siloxycarbonates;
- Polyorganosiloxanes;
- Polyboronorganosiloxanes, -siloxycarboranes and -silazasiloxy-carboranes;
- Polyorganosilazasiloxanes with linear, cyclolinear and polycyclic structure of macromolecules;
- Polyorganocarbosiloxyarylenes etc.

The kinetics and mechanism of the combined polymerization-condensation processes have been investigated [3–5].

DISCUSSION

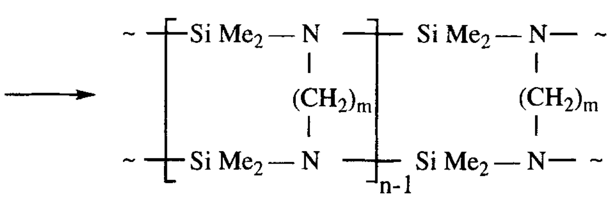
The first efforts aimed at obtaining polymers with inorganic and organo-inorganic molecule chains by using combined polymerisation and condensation processes were published in the 60s. While studying reamination of octamethylcyclotetrasilazane with diaminobenzidine in 1963 we found [7] that when the reaction mixture was heated above the melting point of benzidine (> 120°C), the reaction went on not only opening a silazane cycle, but also releasing ammonia and gradually increasing viscosity by the following scheme:



The resultant solid polymer with $\eta_{red.} = 0.215$ is well soluble in chloroform, dimethylformamide, aniline, pyridine.

In the same year D. J. Zhinkin *et al.* [8] demonstrated that a similar polymerization-condensation scheme occurred in a reaction between organocyclosilazanes and aliphatic diamines, the reaction mixture being heated up to 160 – 200°C:

$$n[Me_2SiNH]_3 + 1{,}5n\ H_2N(CH_2)_mNH_2 \xrightarrow[-n\ NH_3]{}$$



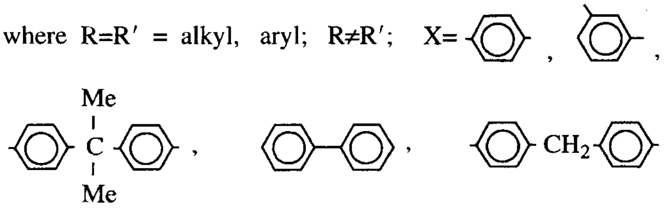
A catalytic amount (0.1 – 1%) of ammonium sulphate accelerates the reaction by more than order of magnitude. Reduction of diamine basicity (elongation of the hydrocarbon fragment between the amino-groups) enhances the catalyst action upon the reaction rate.

R. Elliot and L. Breed [9] used aromatic diols instead of diamines in a reaction with organocyclosilazanes to achieve polymerization condensation. It appeared that with an equimolar ratio of the original reagents the reaction proceeded quite intensely both in block, and in a solvent (toluene, benzene, xylene) releasing ammonia and forming high-molecular compounds with Si—N links in a chain:

$$n[RR'SiNH]_3 + n\ HO{-}X{-}OH \xrightarrow[-(n-1)\ NH_3]{}$$

$$\longrightarrow H_2N \left[(SiRR'NH)_2\ SiRR'{-}O{-}X{-}O \right]_n H$$

where R=R' = alkyl, aryl; R≠R'; X=



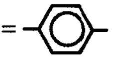
The boiling of synthesized organosilazaoxyarylene polymers with ethyl alcohol during one hour does not lead to any noticeable reduction of viscosity, and their destruction starts only at 350 – 400°C.

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 the residues of the aromatic diol, thereby producing relatively low-molecular products of the siloxyarylene structure [10]:

$$n[RR'SiNH]_3 + 3n\,HO{-}X{-}OH \longrightarrow$$

$$\longrightarrow H_2N\left[SiRR'{-}O{-}X{-}O\right]_n H + (3n-1)\,NH_3$$

$n = 20 \div 25$; R=Me, R′ = Ph; R = R′ =Me, Ph; X=



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

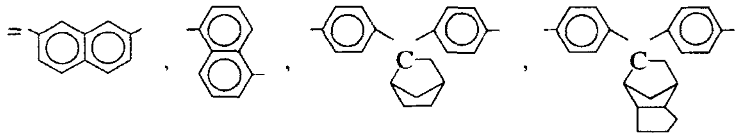
An investigation of reaction of organic diols of different structures with organocyclosilazanes of different cycle sizes and different nature of organic radicals at silicon atoms was aimed at clearing up the effect of diol and organocyclosilazane structures upon the polymerization-condensation process [11]. A reaction of dialkyl-, methylphenyl- and diphenylcyclosilazanes with dioxynaphthalenes and polycyclic bisphenols of the card type proceeded in block until the ammonia isolation stops. With an equimolar ratio of the reagents the reaction proceeds as follows:

$$m[RR'SiNH]_n + m\,HO{-}X{-}OH \xrightarrow[-(n-p)\,NH_3]{}$$

$$\longrightarrow \left[(SiRR'NH)_p{-}SiRR'{-}O{-}X{-}O\right]_m ,$$

where $n = 3$, $R = R' =$ Me, Et, Ph; $R =$ Me, $R' = n-$Bu, -Okt, Ph; $n = 4$, $R = R' =$ Me; $p = 1.2$;

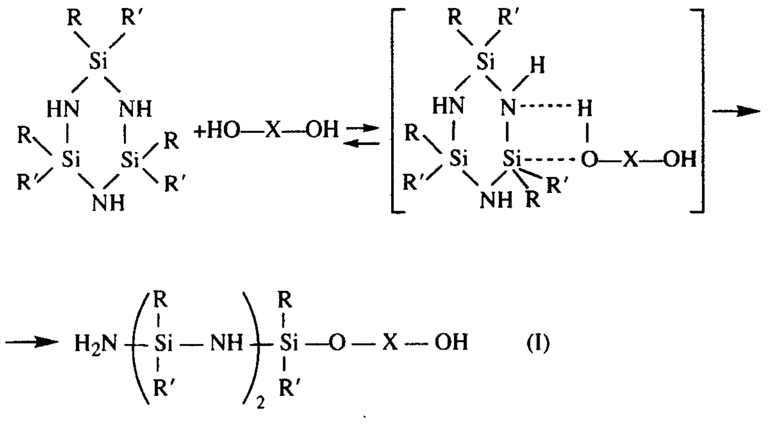
X =



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

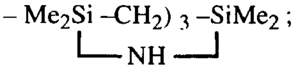
In all the cases at the initial stage of the reaction the kinetic curves of ammonia isolation (Figs. 1, 2) reveal an induction period, its length growing with the radical volume in the silicon atom.

At the initial stage of the reaction the induction period seems to depend on the establishment of a stationary concentration of the transition complex [3] which then decays in the following way:

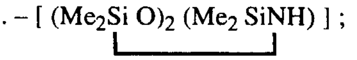


(I)

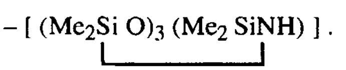
The resultant compound I attacks new molecule of the cycle, forming a similar complex which then either under goes decay or starts a condensation reaction with the new diol molecule. Consequently, the growth of a polymer chain is due both to the polymerization reaction of cyclic silazane proceeding with 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.

1. 

$$-\underbrace{\mathrm{Me_2Si{-}CH_2)_3{-}SiMe_2}}_{\mathrm{NH}}\,;$$

2. 

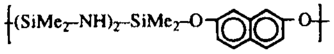
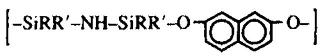
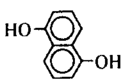
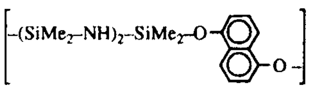
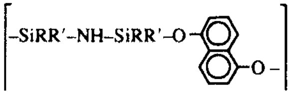
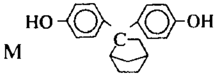
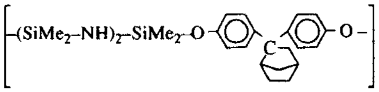
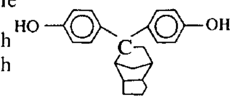
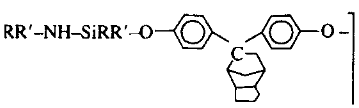
$$-[\underbrace{\mathrm{(Me_2Si\,O)_2\,(Me_2\,SiNH)}}]\,;$$

3. 

$$-[\underbrace{\mathrm{(Me_2Si\,O)_3\,(Me_2\,SiNH)}}]\,.$$

As it's evident from Table I, conversion over ammonia, in some cases, exceeds the one calculated from the quantity of the original diol.

TABLE I Conditions of reaction of organocyclosilazanes with dioxynaphthalenes and polycyclic bisphenols (1:1) and some characteristics of the resultant polymers

$[RR'SiNH]_3$		Diol	Reaction temp., °C	Reaction time, hr	% of isolated NH_3	Elementary link formula	Polymer yield, %	η_{sp} of 1% toluene solution	T_m, °C
R	R'								
Me	Me		130	0.52	101		89	1.29	8
Me*	Me*		130	0.6	100		73	0.75	
Me	Ph		140	1.0	106			0.82	27
Ph	Ph		170–180	2.0	84		–	0.32	
Me	Me		130	0.5	100		90	1.01	−10
Me*	Me*		130	0.6	91		74	0.69	
Me	Ph		140	1.2	97		83	0.50	30
Ph	Ph		160–170	2.2	81			0.23	
Me	n.-Bu		180	0.5	101		89	0.58	−13
Et	Et		180	0.8	101		81	0.60	−25
Me	n.-C_8H_{17}		180	1.0	100		91	0.45	−42
Me	M		130	1.5	100		96	0.81	36
Me	Me		140–150	1.2	97		95	0.80	–
Me	Ph	 X)	130–150	2.0	98		96.5	0.40	56
Ph	Ph		170–180 $[Me_2SiNH]_4$	3.0	94		–	0.34	63

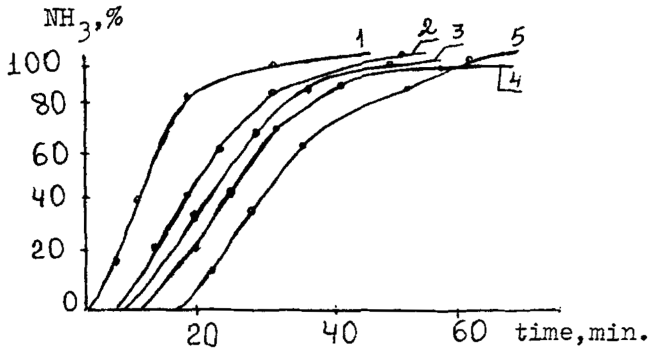


FIGURE 1 Relation of the isolated ammonia amount to the time of reaction of 1,5-dioxynapthalene and $[RR'SiNH]_3$ 1;1 ratio and at temperatures listed in Table I. 1 – R = R' = Me; 2 – R = Me; R' = *n*–Bu; 3 – R = R' = Et; 4 – R = Me, R' = Ph; 5 – R = Me, R' = C_8H_{17}.

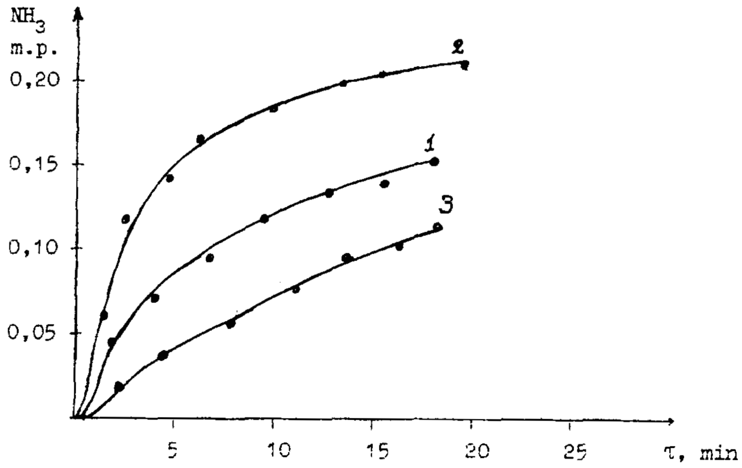
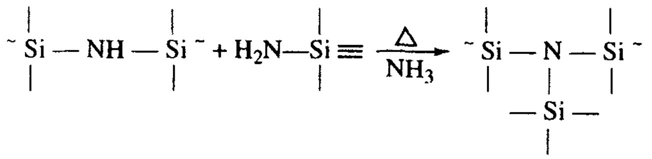


FIGURE 2 Comparison of the theoretical curves of separation of ammonia with the experimental data of the interaction of phenol with:
1.—$Me_2Si - (CH_2)_3 - SiMe_2$; 2.—$[(Me_2SiO)_2(Me_2SiNH)]$; 3.—$[(Me_2SiO)_3(Me_2SiNH)]$.
NH

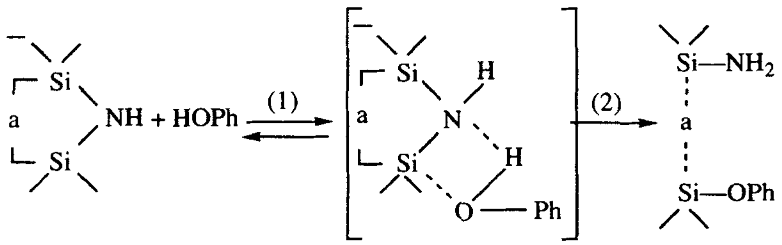
When conversion over ammonia was less then one mole on mole of the initial diol, the reaction had been continuing up to 1.03 – 1.05 moles of NH_3 on one mole of the diol. The polymers transformed into unsoluble, unfusible state. These facts demonstrated, that not only the reaction of chain increase occurs, but also the reaction of reaminiation takes place due to the interaction of NH_2-groups, being formed during the process of chain increase, with $\equiv Si—NH—Si\equiv$ groups presenting into the system. It causes formation of branching and retina macromolecules with trisilylaminogroups at the knots of branching:



$$\sim Si—NH—Si\sim + H_2N—Si\equiv \xrightarrow[NH_3]{\Delta} \sim Si—\underset{\underset{|}{—Si—}}{\overset{|}{N}}—Si\sim$$

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 generalities of CPC process [3]. Considering the above mantioned 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 further heterofunctional condensation of the formed NH_2-groups with hydroxy-groups did not lead to any satisfactory approximation at solving the extremal problem.

At the given precision of the experiment the most satisfactory result from the point of view of minimization of average deviation (Fig. 2) is the following mechanism:



$$\equiv SiNH_2 + HOPh \xrightarrow{(3)} \overset{(A)}{\equiv SiOPh + NH_3}$$

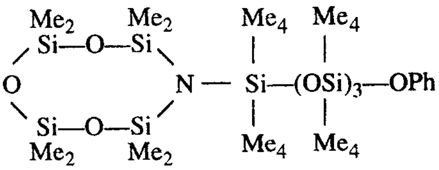
$$PhOH + NH_3 \overset{(4)}{\rightleftharpoons} PhO^-(NH_4)^+ \qquad (B)$$

$$(\equiv Si)_2NH + H_2NSi \equiv \xrightarrow{(5)} (\equiv Si)_3N + NH_3$$

$$2 \equiv SiNH_2 \xrightarrow{(6)} \equiv Si-NH-Si \equiv + NH_3$$

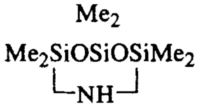
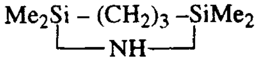
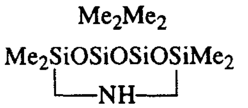
The velocity constants of the elementary stages were determined (Tab. II) by minimizing the average deviation of the points of the experimental curve from the theoretical function of separation of ammonia.

The formation of transition complex have been established by 'H—NMR method [3]. The proceeding of the reaction of reamination (stage 5) was stated with the experiment. Hence by using the data of 'H—NMR—, UR—spectra and chromatography analysis the compound of the following structure was shown to form:



The kinetic data reveal (Tab. II) 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) 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 catalysed by nucleophilic particles (B), thus leading to macromolecu-

TABLE II* The velocity constants of the elementary stages of CPC

Si — N containing heterocycle	$K_{1.2}$	K_3	K_5	K_6
 $Me_2SiOSi(Me_2)OSiMe_2$–NH–	1.20	20.31	0.68	0.94
 $Me_2Si-(CH_2)_3-SiMe_2$–NH–	0.20	10.12	1.04	0.94
 $Me_2SiOSi(Me_2)OSi(Me_2)OSiMe_2$–NH–	0.05	13.19	1.10	0.90

* $[K_i] = min^{-1}$.

lar chain branching and, eventually, to polymer structuration. Indeed, when a polymer mass is subjected to prolonged heating up to 180 — 200°C, the polymers change to a nonmelting and insoluble state.

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

Methylphenyl- and diphenylcyclosilazanes form polymers with higher temperatures of vitrification (Tab. I). In the case of organocyclosilazanes with large aliphatic radicals at silicon atoms highly viscous liquids are formed.

It is noteworthy that the importance of 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 vitreus; in such a case, just as in [10], there form products in which an elementary link does not contain silazane-groups and which are of a high-molecular weight ($\eta_{sp} = 0.09 - 0.13$).

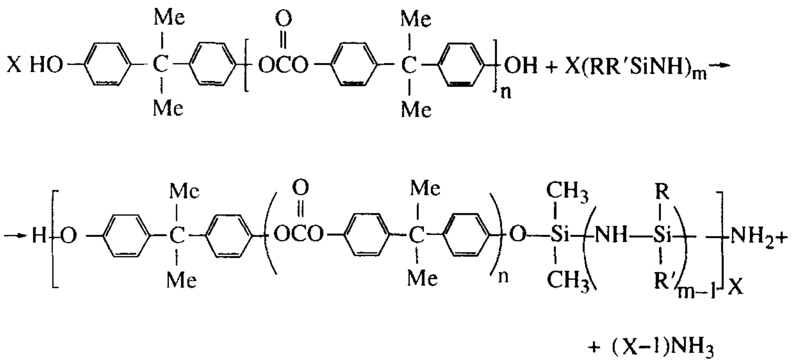
Polymers based on diorganocyclosilazane and aromatic diols are readily soluble in benzene, toluene, chloroform, but insoluble in saturated hydrocarbons.

The character of polymer thermomechanical curves depends on the ratio of the original compounds, the volume of radicals at silicon atoms and the aromatic diol nature. When the permanently applied load is increased (from 30 to 100 g), 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 ($T_{vit} = +38 \div +93$°C).

According to the thermogravimetric data, mass losses, as low as 2–5% were observed in polymers obtained from hexamethylcyclotrisilazane and aromatic diols at an equimolar ratio and at 400°C.

The results on polymerization condensation of organocyclosilazanes with oligocarbonate diols (OCD), published recently by A.A. Zhdanov, N.G. Lekishvili *et al.* [12], prove the importance of the conditions of the reaction for the process and the structure and molecular mass of the resultant polymers (Tab. III).

Reaction of organocyclosilazanes and OCD in the boiling $CHCl_3$ solution goes on by the following theoretical scheme:



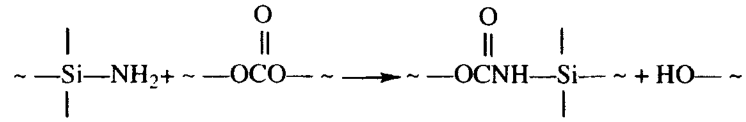
reaching maximum molecular masses (MM) of polymers with a regular polyblock structure. However, the reaction proceeds slower under the described conditions and an output of 1 mole of NH_3 per 1 mole of the initial cycle is reached not before 26–30 hours (Tab. III). In this case chloroform acts not only as a solvent, but also as a protonodonor reagent: its association with cyclic silazane and the blocking of the nitrogen atom electronic pair weaken the Si—N link and facilitate

TABLE III Conditions of reaction between organocyclosilazanes and OCD and some characteristics of the resultant polymers

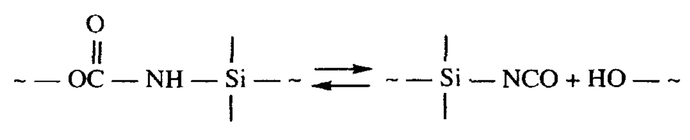
$[RR'SiNH]_m$	*n in OCD*	*Conditions of reaction*	*Reaction temp., °C*	*Reaction time, hr*	*Amount of NH_3 mole/mole/cycle*	*[η] dl/g*	$T_{vit.}$, *°C*
$[Me_2SiNH]_3$	8	In mass	130–160	0.8	0.98	0.30	–
	8	15% solution in $CHCl_3$	60	26.0	1.02	0.72	124
$[Me_2SiNH]_4$	8	In mass	160–170	1.5	0.88	0.22	–
	8	15% solution in $CHCl_3$	60	30.0	1.04	0.78	134
$[MePhSiNH]_3$	8	In mass	170–180	1.6	0.88	0.45	–
	12	In mass	190–200	2.5	0.78	0.33	–
	16	In mass	200	3.0	0.73	0.22	–
	8	In mass	250	3.0	1.19	0.30	–
	8	15% solution in $CHCl_3$	60	26.0	0.42	0.62	167

its subsequent breakage by the OCD hydroxyl-group. Under the same conditions a less basic methylphenyl cyclotrisilazane reacts with OCD at a rate twice as slow as hexamethylcyclotrisilazane.

It is evident from Table III that the process goes on at a considerable higher rate in mass; however, side reactions reduce the MM and cause a less orderly structure of the polymer due to the crushing of polycarbonate and silazane blocks, and give rise to urethane and isocyanate groups in a macrochain formed by the following schemes:

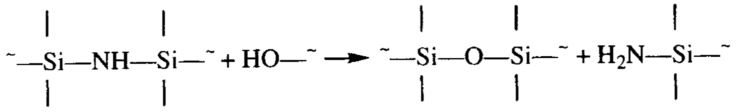


$$\sim\text{—}\underset{|}{\overset{|}{\text{Si}}}\text{—NH}_2 + \sim\text{—O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{O—}\sim \longrightarrow \sim\text{—O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NH—}\underset{|}{\overset{|}{\text{Si}}}\text{—}\sim + \text{HO—}\sim \qquad (1)$$



$$\sim\text{—O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—NH—}\underset{|}{\overset{|}{\text{Si}}}\text{—}\sim \rightleftarrows \sim\text{—}\underset{|}{\overset{|}{\text{Si}}}\text{—NCO} + \text{HO—}\sim \qquad (2)$$

These side reactions become particularly effective with greater OCD length, i.e., when the relative content of ester groups grows. Therefore, when the degree of polycondensation (n) of the initial OCD increases in case of a reaction in mass with methylphenylcyclotrisilazane, the resultant polymer MM and conversion over ammonia decrease (Tab. III) at the expense of an increased NCO—groups concentration. At higher temperatures (250°C) the following side reaction acquires significance:



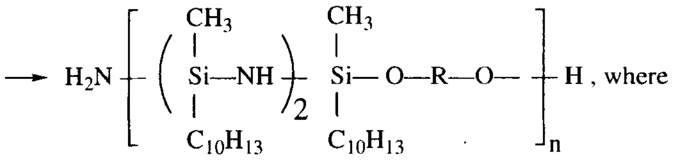
$$\sim\!\!-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{NH}-\underset{|}{\overset{|}{\mathrm{Si}}}-\!\!\sim + \mathrm{HO}-\!\!\sim \longrightarrow \sim\!\!-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\!\!\sim + \mathrm{H_2N}-\underset{|}{\overset{|}{\mathrm{Si}}}-\!\!\sim \quad (3)$$

due to the rightward shift of the reaction (2) equilibrium causing an increase of concentration of OH-groups capable of reacting with less reactable NH-groups in the chain linear section. As a result there arises a possibility of condensation processes leading to an additional NH_3 isolation.

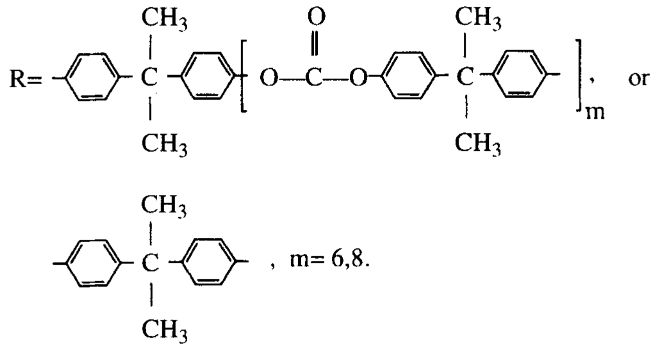
The obtained polymers are solid substances soluble in polar solutions, although limitedly soluble in aromatic hydrocarbons.

We used [13, 14] methylcyclotrisilazane with tricyclodecenyl groups (TDCTS) at silicon atoms, as a partner of oligocarbonate diol (OCD) to investigate the effect of radicals set at silicon atom upon the CPC process. It turned out that the reaction proceeds also via the mechanism of polymerization-condensation by the general scheme:

$$n[\mathrm{CH_3(C_{10}H_{13})\,SiNH}]_3 + n\ \mathrm{HO-R-OH} \xrightarrow[-\,(n-1)\,\mathrm{NH_3}]{\Delta}$$



$$\longrightarrow \mathrm{H_2N}\left[\left(\underset{\mathrm{C_{10}H_{13}}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{NH}\right)_2 \underset{\mathrm{C_{10}H_{13}}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O-R-O}-\right]_n \mathrm{H}, \text{ where}$$

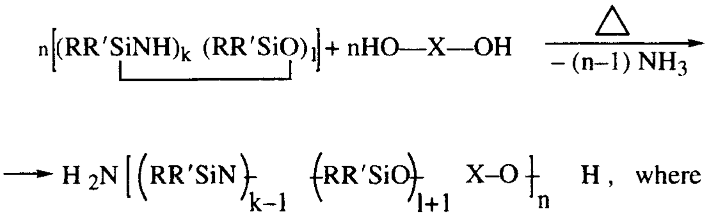


R=, or, m=6,8.

Differing from [13], where diemthyl-(HMCTS) and methylphenylcyclotrisilazanes were selected as Si—N-containing heterocycles the reaction in mass proceeds more slowly and block-copolymers formed are of considerably low molecular mass ($\eta_{sp} \approx 0.1$).

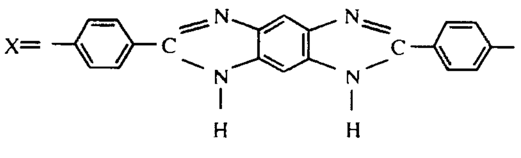
There have been investigated some of the kinetic regularities of this reaction [15, 16]. On the base of calculation of the velocity constants of the elementary stages of CPC there was ascertained that the limiting stage of the reaction, as in case of HMCTS, is the one of forming the transition complex (1) and the opening of heterocycles (2). But the induction period of the reaction determined by the constants of (1) and (2) stages is longer for TDCTS than the one for HMCTS [15]. The side stage of reamination, what leads to the forming of the polymers of branching structure is of insignificant "specific weight" and probably is accelerated in the range of maximum of concentration of Si—NH_2 groups. That's why the formation of unsoluble and unfusible products is observed only when this reaction is carried out at rigid conditions [14, 15].

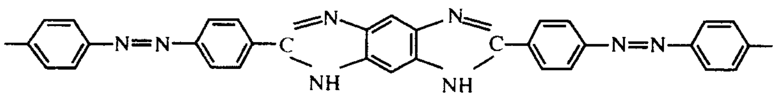
We also synthesized polyorganosilazasiloxyheteroarylenes by using the reaction of CPC of different silicon-nitrogen containing heterocyles with benzimidazol bisphenols [17]:



$$n\left[(RR'SiNH)_k\,(RR'SiO)_l\right] + nHO{-}X{-}OH \xrightarrow[-(n-1)\,NH_3]{\Delta} H_2N\left[\left(RR'SiN\right)_{k-1}\left(RR'SiO\right)_{l+1} X{-}O\right]_n H, \text{ where}$$

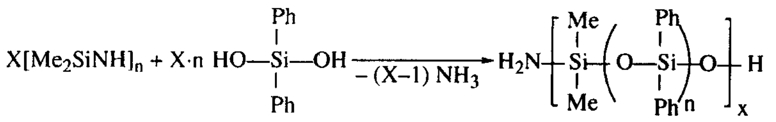
$R = R' = CH_3$, $R = CH_3$, $R' = C_6H_5$, $k = 1 \div 2$, $l = 0 \div 2$,





The solid, colored film-forming, soluble in aprotonic amidic dissolvents polymers were obtained. They are more thermostable (Fig. 3) than polyorganosilazasiloxycarbonates on the basis of OCD. Some of them are recomended as modifing filers for producing antifrictional autolubricating composites.

A polymerization polycondensation process can be carried out using organic diamines and diols, as well as organosilicon diols. Thus, a reaction of diorganocyclosilazanes with a three-four-fold molar excess of dihydroxydiphenylsilane yielded polyorganosiloxanes with a high content of diphenylsiloxy links in a polymer chain [18]:

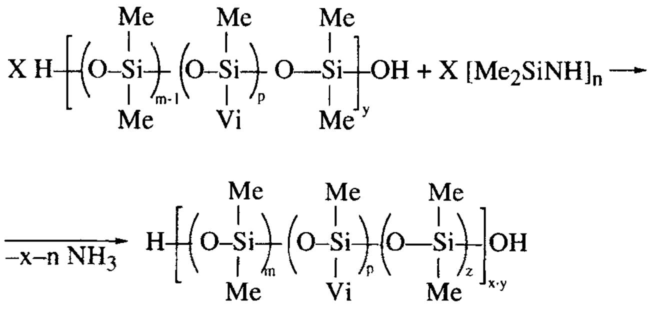


$$X[Me_2SiNH]_n + X\cdot n\, HO-\overset{Ph}{\underset{Ph}{Si}}-OH \xrightarrow[-(X-1)\,NH_3]{} H_2N\left[\overset{Me}{\underset{Me}{Si}}\left(O-\overset{Ph}{\underset{Ph}{Si}}\right)_n O\right]_x H$$

where $n=3$ or 4.

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

Practically curious results have been recently obtained in a study of a reaction between α,ω-dihydroxypolydimethyl (methylvinyl) siloxanes and dimethylcyclosilazanes [20]. The reaction also proceeded according to the polymerization polycondensation mechanism with ammonia isolation:



$$X\,H\left[\left(O-\overset{Me}{\underset{Me}{Si}}\right)_{m-1}\left(O-\overset{Me}{\underset{Vi}{Si}}\right)_p O-\overset{Me}{\underset{Me}{Si}}\right]_y OH + X\,[Me_2SiNH]_n \longrightarrow$$

$$\xrightarrow[-x-n\,NH_3]{} H\left[\left(O-\overset{Me}{\underset{Me}{Si}}\right)_n\left(O-\overset{Me}{\underset{Vi}{Si}}\right)_p\left(O-\overset{Me}{\underset{Me}{Si}}\right)_z\right]_{x\cdot y} OH$$

Therefore, the molecular mass of polydimethyl (methylvinyl)-siloxanes increases forming high-molecular elastomers ($[\eta] = 1.4 - 1.8$ dl/g). The optimal conditions of the process require the reaction tem-

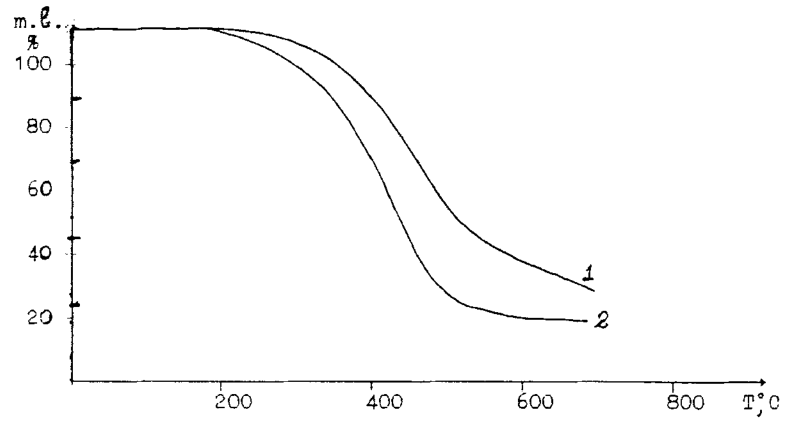
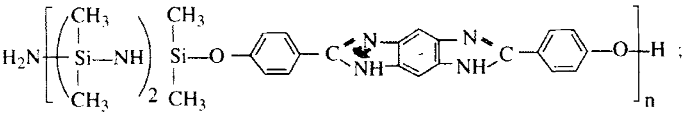
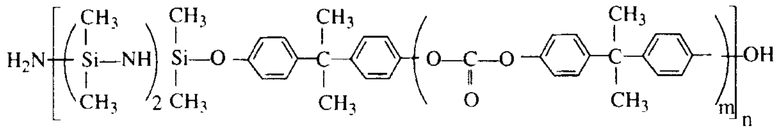


FIGURE 3 The curves of thermogravimetrical analysis of the polymers:

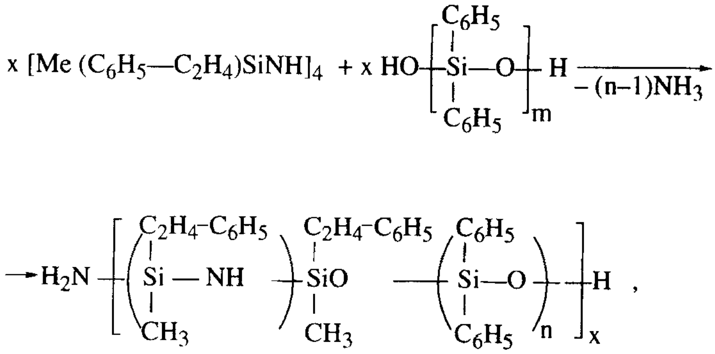
1.


2.


perature 175°C and the diol-to-hexamethylcyclotrisilazane ratio 1:2. The lower the temperature, the slower the reaction rate; meanwhile, at higher temperatures the formed polymer has an insufficient MM because hexamethylcyclotrisilazane 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 α,ω-dihydro-poly-dimethyl (methylvinyl) siloxanes MM. The characteristic viscosity in toluene observed in the diol condensation product at MM = 6000 was 0.5 dl/g after 10 hours, 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 (methylvinyl) siloxane, since the rubber obtained by polymerization polycondensation of dihydroxypolydimethyl (methylvinyl) siloxanes with dimethylcyclosilazanes without acid or an alkaline catalyst, is, naturally, free of the latter remains which usually deteriorate the thermal stability of rubber.

There are investigated [19] the reactions of tetramethyltetraphenethylcyclotetrasilazanes with dihydroxydiphenylsilane and 1,3-dihydroxy-tetraphenyldisiloxane at the molar ratio 1:1. The processes are established to proceed via polymerization-condensation mechanism releasing ammonia and forming corresponding polyorganosilazaoxanes by the scheme:



$$x\,[\mathrm{Me}(C_6H_5{-}C_2H_4)\mathrm{SiNH}]_4 + x\,\mathrm{HO}{\left[\overset{C_6H_5}{\underset{C_6H_5}{\mathrm{Si}}}{-}\mathrm{O}\right]_m}\mathrm{H} \xrightarrow[-(n-1)NH_3]{} H_2N{\left[\left(\overset{C_2H_4{-}C_6H_5}{\underset{CH_3}{\mathrm{Si}}}{-}\mathrm{NH}\right)\overset{C_2H_4{-}C_6H_5}{\underset{CH_3}{\mathrm{SiO}}}\left(\overset{C_6H_5}{\underset{C_6H_5}{\mathrm{Si}}}{-}\mathrm{O}\right)_n\right]_x}\mathrm{H}\ ,$$

where m=0 or 1.

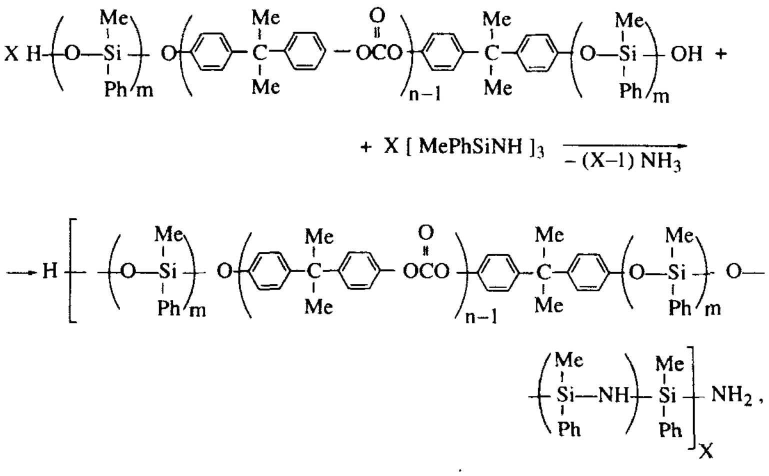
The reaction doesn't proceed even at 130–140°C, when it's carried out in aromatic solvent (toluene, ditolylmethane) due to high hydrolytic stability of cyclosilazane with phenethyl radical set at silicon atom, while in mass the beginning of this reaction is already observed at 70°C achieving the maximum 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's noticeable in case of the reaction with 1,3-dihydrotetraphenyldisiloxane, which leads to decrease of nitrogen-content in the polymer, after it's vacuumized, due to replacing of silazanic bonds by siloxanic ones.

Investigation of kinetics of the reaction monitors the process to be characterized by induction achieving 30 min. in case of the reaction with dihydroxydiphenilsilane at 98°C, while when increasing temperature above 130°C, it diminishes to 3 min. $\bar{M}_n$ of the polymers is of the rate of $6.0 \div 6.7 \cdot 10^4$. Gelchromatographic analysis demonstrates sufficiently narrow distribution of MM in the polymers.

Combined polymerization-condensation reaction of tris (tricyclodecenylmethyl) cyclotrisilazane with the oligodimethylsiloxanes (m = 12, 35, 72) at ratio 1:1 [13] was also investigated and the process was established to be also affected by the length of oligomeric chain (Tab. IV) [14].

As it's evident from the data of Table III, increasing extent of polymerization of the oligomer, temperature and the duration of the reaction also increase as well as degree of conversion in terms of ammonia and the yield of polyorganosilazasiloxanes, while their vitrification temperature decreases.

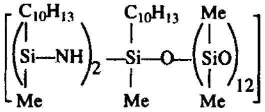
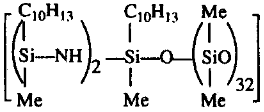
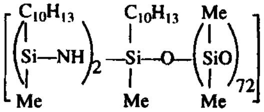
A polymerization-condensation reaction of oligocarbonatesiloxanedils (OCSD) with trimethyltriphenylcyclotrisilazane yielded polycarbonatesilazasiloxane (PCSS) block-copolymers [6]:

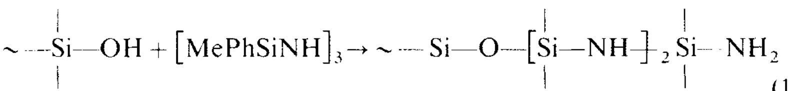


where n = 14, 24, 39, 49, 57, 69, m = 3, 6, 9, 15, 30, 60.

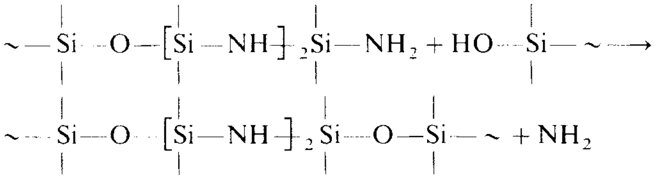
The reaction went on in block at 180°C until complete ceasing of ammonia isolation. The ammonia isolation is indicative of polymerization as well as polycondensation proceeding in accordance with the following schemes:

TABLE IV Conditions of the reaction of tris (tricyclodecenylmethyl) cyclotrisilazane with α,ω-dihydroxyoligodimethylsiloxanes and some properties of the synthesized polymers

Original oligomer	$T_{reac.}$, °*C*	t_r *hrc*	*Am. of* NH_3 *%*	T_g, −°*C*	*Elementary ring of polymer*	*Yield of polymer, %*	η_{sp}
$HO{-}[SiMe_2O{-}]H_{12}$	150–160	1,5	80	78		79	–
$HO[SiMe_2O]H_{32}$	170–180	2,5	85	100		82	–
$HO[SiMe_2O]H_{72}$	210–220	4,0	90	102		89	0,3



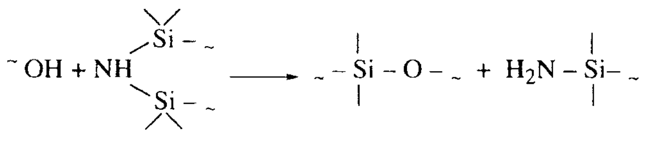
$$\sim -\mathrm{Si}-\mathrm{OH} + [\mathrm{MePhSiNH}]_3 \rightarrow \sim -\mathrm{Si}-\mathrm{O}-[\mathrm{Si}-\mathrm{NH}]_2\mathrm{Si}-\mathrm{NH}_2 \qquad (1)$$



$$\sim -\mathrm{Si}-\mathrm{O}-[\mathrm{Si}-\mathrm{NH}]_2\mathrm{Si}-\mathrm{NH}_2 + \mathrm{HO}-\mathrm{Si}-\sim \longrightarrow$$

$$\sim -\mathrm{Si}-\mathrm{O}-[\mathrm{Si}-\mathrm{NH}]_2\mathrm{Si}-\mathrm{O}-\mathrm{Si}-\sim + \mathrm{NH}_2 \qquad (2)$$

The molecular masses of the formed polymers undergo changes antibate to conversion in terms of ammonia depending upon the length of the siloxane part of OCSD macromolecule elementary link, this occurring at a high concentration of functional groups, i.e., the amount of released ammonia exceeds its rated value at low m-values in OCSD. Both these data and the IR analysis data (absorption bands appearing with the maximum of 2285 cm^{-1} which is typical of the NCO-groups) indicate that the reaction of OCSD and cyclic silazane in ambiguous, and the macromolecule structure comprises also isocyanate groups, like in schemes 1 and 2 on page 11. The equilibrium of reaction 2 (page 11) will shift rightwards if the OCSD hydroxyl groups react with the silazane link not only in a cycle, but also in a linear chain:



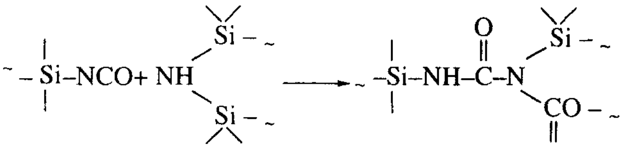
(3)

The latter reaction proceeds more readily at a higher hydroxyl-group concentration, i.e., at a lower m-value in OCSD, and in the presents of an anion-type catalyst which forms as a result of reaction between the hydroxyl groups and the released ammonia (K. A. Andrianov, N. G. Lekishvili *et al.* [21]):

$$\sim - \mathrm{OH} + \mathrm{NH}_3 \rightleftharpoons \sim - \bar{\mathrm{O}}(\overset{+}{\mathrm{N}}\mathrm{H}_4) \qquad (4)$$

At high m-values, the rate of reaction between hydroxyl-groups and silazane links in a linear chain reaction (3) is significatly lower, the Si—NCO— groups forming reaction equilibrium (reaction 2, page 14) is shifted leftwards; hence, higher MM of the end polymers are achieved.

The branching and binding mechanism in the reacting system can be shown schematically as



(5)

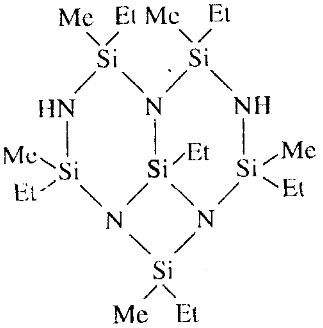
Thus, the scheme of PCSS formation presented on page seems to be an ideal one, because the resulting block-copolymers, containing not only polycarbonate and silazasiloxane blocks, but also urethane groups in a chain, have branched macromolecular structure.

The two-phase structure of synthesized polycarbonatesilazasiloxane block-copolymers was proved by electron microscopy and X-ray analyses.

The polymerization polycondensation method turned out to be a sufficiently universal one for synthesizing polymers with inorganic and organo-inorganic molecular chains of various composition and structure, because it can employ organocyclosilazanes as well as organocyclosilsesquiazanes, mixed organocyclosiloxazanes, organocyclosiloxanes and organocyclosilsesquioxanes as the initial cyclic compound, which can readily entrain comparatively low-reactable different organic and organosilicon diols into polymerization polycondensation reactions.

Keeping in mind the dependence of the polymerization polycondensation reaction on the structure and reactability of the original organosilicon heterocycles and diols, an investigation [21,22] was carried out into the interaction of polycyclic organocyclosilsesquiazanes with α,ω-dihydroxydimethylsiloxanes, dihydroxydiphenylsilane and tetrahydroxystetraphenylcyclotetrasiloxane (tetrol).

An interaction of pentamethylhexaethyltricyclohexasilpentazane of the following structure [21]:



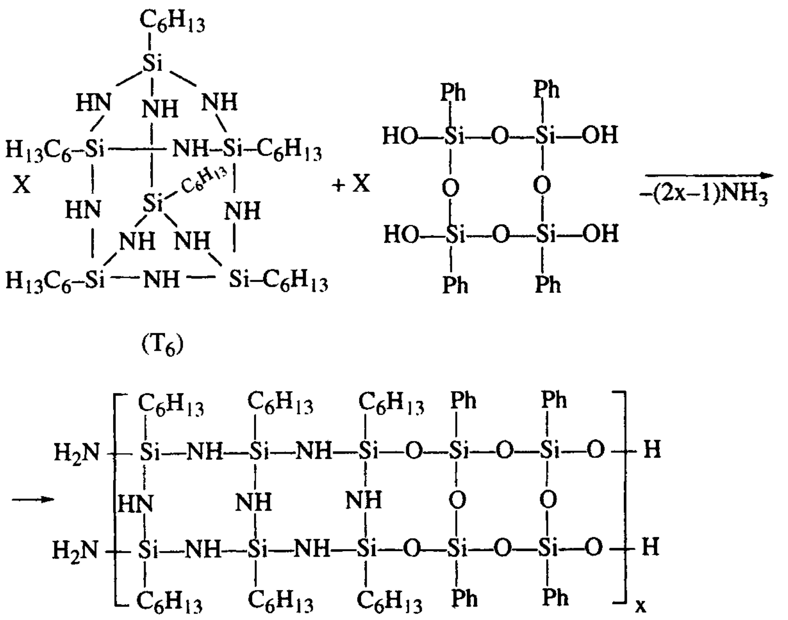
(I)

with α,ω-dihydroxyoligodimethylsiloxanes (n = 10.42) and dihydroxydiphenylsilane in block at 170–180°C and at an equimolar ratio of the reagents has evidenced that the reaction goes on according to a matched polymerization polycondensation scheme with ammonia isolation, however forming structurized polymers. Meanwhile, although the conversion in terms of ammonia is as a rule close to the quantitative in the reaction of organocyclosilazanes and diols, it does not exceed 50% when diols react with a tricyclic compound I. In the latter cased the initial stage of the reaction shows a long induction period and a slow growth of MM within the first 3–6 hours. Here, just as in case of organocyclosilazanes, a silazane cycle opens initially along the Si—Nh—Si link to form a Si—O link and an NH_2-group which starts a condensation reaction with the hydroxyl group of another diol molecule. Since a tricyclic compound contains two reaction centres in different cycles, and each chemical event of opening a silazane ring gives rise to a new, more reactive NH_2-group, there immediately appears a possibility of forming a branched oligomer with its subsequent structurization. The reaction is a slow one, limited by the stage of cycle openings. Only a prolonged heating of the reaction staff 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 hexylsilsesquiazane (T_6) with α,ω-dihydroxyoligodimethylsiloxane (n = 42) proceeds at a much higher rate. A great number of branching centres, 8 of them, in the complex molecule of cyclosilsesquiazane T_6 ensures structurization of the system within 2 hours at 150°C and 10 minutes at 180°C.

The polymerization polycondensation of complex cyclosilsesquiazane systems with organosilicon diols proceeding up to gelformation, yields viscous, soluble liquids which after structurizaton form rubber-like substances, the vitrification temperature of which shifts to the negative temperature region and the elasticity module decreases with a longer siloxane chain.

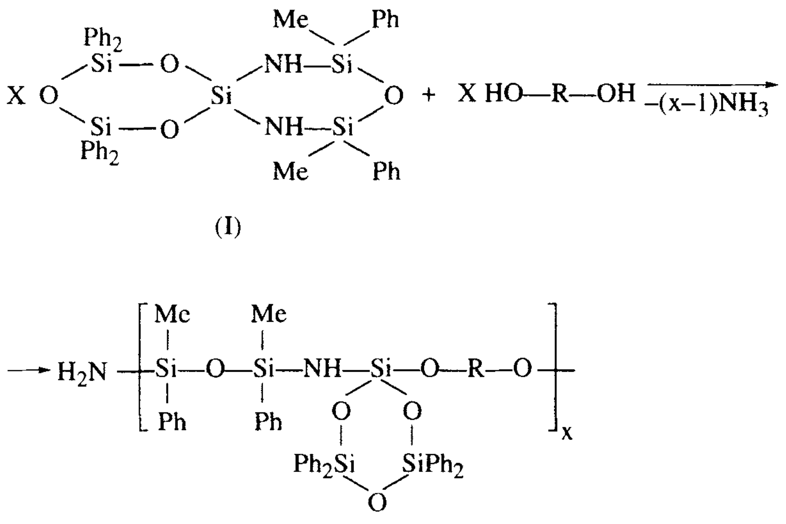
An increase of functionality of the original hydroxyl-containing organosilicon compound from 2 to 4 in a polymerization polycondensation reaction does not lead to any increase in the three-dimensional process rate and in the gel-fraction output. Thus, the reaction of cyclosilsesquiazane T_6 with tetrol proceeds under the same conditions (170–180°C, reagents ratio 1:1) in block within 15 hours with a 70% conversion in terms of ammonia and ~ 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 hours, 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 [21]:



However, an incomplete ammonia release and presence of comparatively great number of functional groups evidence for some defects in the structure, and a low viscosity value ($\eta_{red.} \simeq 0.1$) at MM = 218000 and asymmetry coefficient $z \simeq 5$ indicate to a branched structure of macromolecules. The polymer is an amorphous powder with $T_{vit} \sim 100°C$, showing no region of the high elastic state. Therefore, in this case polymerization polycondensation is accompanied by cyclization processes and yields a branched polymer with cyclolinear fragments in a macromolecule.

Owing to the different reactivity of Si—N and Si—O bonds with respect to hydroxyl-containing compounds a special research was carried out [23, 24] to investigate polymerization polycondensation of mixed cyclosilazasiloxanes, viz., organospirobicyclosilazasiloxanes with organic, carborane and organosilicon diols of different structures.

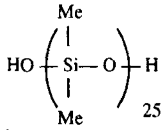
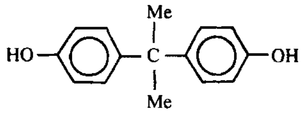
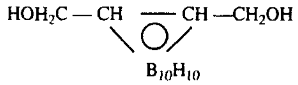
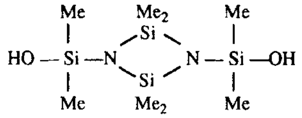
The reaction of organospirobicyclosilazasiloxane (I) with the mentioned diols in block or in solution at an equimolar cycle-to-diol ratio proceeding up to a complete ceasing of ammonia release, appeared in an ideal case to be going on as



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

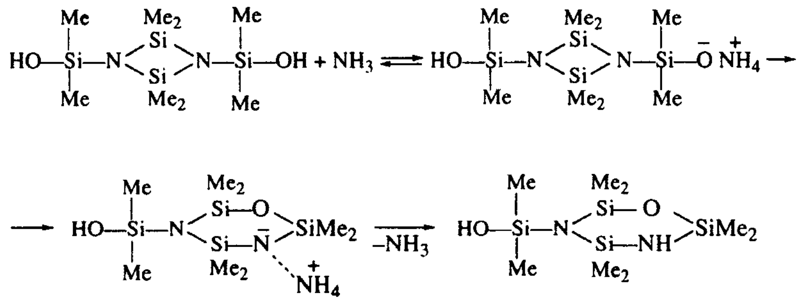
As the data of Table V show, the polymerization polycondensation of α,ω-dihydroxyoligodimethylsiloxane ($n = 25$) with I in block and of diphenylpropane with I, both in block and in toluene, yields mainly insoluble products. When 1,2-bis (hydroxymethyl) carborane reacts with I, a vitreous polymer, readily soluble in benzene and toluene; while when N,N^1-bis(hydroxydimethylsilyl) tetramethylcyclodisilazane reacts with I, a soluble oligomer is formed; however, the conversion in

TABLE V Reaction of organospirobicyclosilazasiloxane (I) with different diols

Diol	*Medium*	*T, °C*	*τ, hr*	*% of isolated NH_3*	*% of gelfraction*
 $HO\left(\overset{Me}{\underset{Me}{Si}}-O\right)_{25}H$	In block	180	5.0	70	66
	In block	150	6.5	86	73
	Toluene	110	3.5	90	31
	Toluene	110	4.5	99	–
	In block	140–200	4.0	48	–
	Toluene	110	9.5	40	–

terms of ammonia is not high either in block 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 particles resulting from a side reaction between diol hydroxyl groups and the released ammonia (p.23 [4]), which catalyses the further process of polymerization condensation. A lower acidity of carborane diol causes a leftward shift of an equilibrium reaction which forms a nucleophilic particle, and, owing to a low concentration of nucleophilic particles the siloxane cycle opens at an insignificant rate; however, the reaction of cycle opening with silazane-groups and condensation of OH- and 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 particles that can open a siloxane cycle is higher in the reaction of silazasiloxane bicycle with dimethylsiloxane and aromatic diols due to a rightward shift of the side reaction and to a less complete reaction resulting from a comparatively rapid formation of a branched and partially network polymer. Therefore, the experimental data prove the decisive role of the diol nature and bicyclosilazasiloxane siloxane cycle activity in the formation of structurized products.

An interesting course of reaction is observed during polymerization polycondensation of bicyclosilazasiloxane with N,N^1-bis (hydroxydimethylsilyl) tetramethylcyclodisilazane. The reaction begins with opening silazane-groups in the bicycle and condensation of the formed end NH$_2$-groups with diol hydroxyl groups. However, as soon as ammonia appears in the reaction system, an anion re-grouping of cyclosilazane begins at a noticeable speed and proceeds with the cycle expansion:

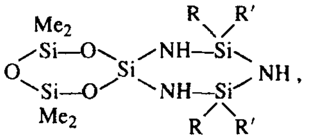


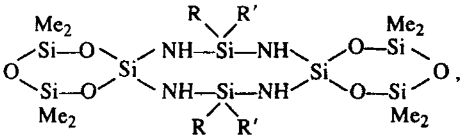
This results in the hydroxyl group concentration drop, and the reaction is less speedy and less complete, while the resultant polymers are of a lower MM.

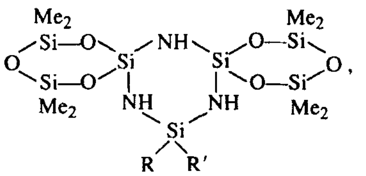
A similar re-grouping of cyclodisilazane accompanied by the cycle expansion and cyclosilazasiloxane formation had been reported earlier by K. A. Andrianov *et al.* in a study of polymerization condensation of N,N^1-bis (hydroxymethylsilyl) tetramethylcyclodisilazane with dimethylcyclosiloxanes at the presence of tetramethylammonium siloxanediolate [26].

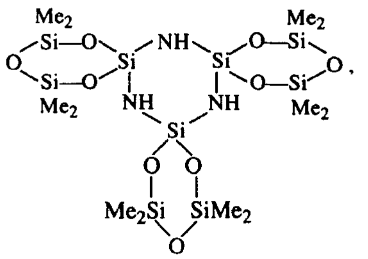
The polymers reported in [23, 24] are of a high thermaloxidative stability. Their mass losses start at 350°C and the basic destruction occurs at temperature above 400°C.

A. A. Zhdanov *et al.* [25] investigated the interaction of α,ω-siloxeanediols with organospirocyclosilazanes (SC) of the new type with following structures:









where R = Me, R′ = Me, Vin.

Here, two main processes are observed to proceed: at 130–140°C an opening of interior cycles occures 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 retina structure are obtained. As the authors consider, 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 of the type of $O^-[NH_4]^+$, formed on the endings of the polymer chain, when increases the concentration (molar ratio) of isolating ammonia NH_3, due to heterofunctional polycondensation:

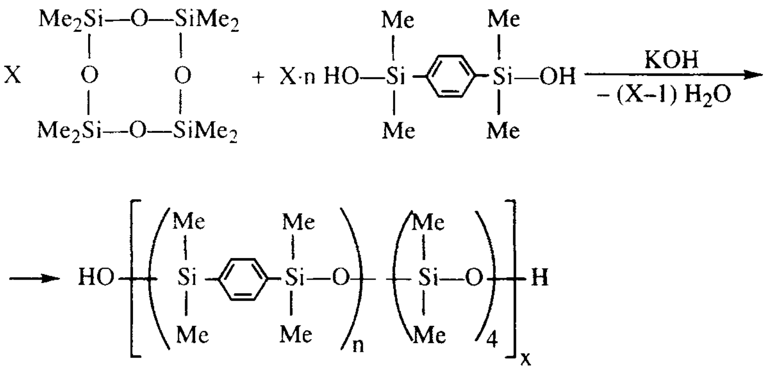
$$\equiv Si-NH_2 + HO-Si\equiv \xrightarrow[-NH_3]{\Delta} \equiv Si-O-Si\equiv$$

$$NH_3 + HO-Si\equiv \longrightarrow NH_4^+\,O-Si\equiv,$$

and there is no requirement of initiators of ionic polymerization. On the basis of the determination of Gel-fractions and of the method of equilibrium swelling there is demonstrated that the density of sewing together of RP essentially depends on the initial ratio of SC-siloxandiol and achieves its maximum at the corresponding one (ratio) of the components.

Although the polymerization polycondensation of organocyclosilazanes and organocyclosilazoxanes with organic and organosilicon diols proceeds actively enough without any anionic initiators owing to the releasing ammonia capable of reacting with diol hydroxyl groups to form nucleophilic particles which catalyse the further process, the reaction of organocyclosiloxanes and diols is impossible without anion initiators.

A reaction of octamethylcyclotetrasiloxane (D_4) with 1,4-bis (hydroxydimethylsilyl) phenylene was studied [27] and proved that D_4 entrains diol into polymerization polycondensation only in the presence of an anion initiator (potassium oxide), producing copolymers with linear molecular chains:



The reaction was carried out in a solution at 150°C and at cycle-to-diol ratios 1:1, 1:4 and 1:10. By fractionating the resulting polymers their copolymer composition was confirmed. Copolymers precipitated from benzene solution by methanol copolymers were, as a rule, white amorphous powders with $\eta_{sp} \simeq 1.5$. They are soluble in aromatic hydrocarbons, ether, CCl_4, but insoluble in the methyl and ethyl alkohols.

Comparatively weakly reactive organic and organosilicon diols are entrained into polymerization polycondensation reaction with organocyclosiloxanes in the presence of nucleophilic initiators at the expense of a rapid exchange reaction between the diol hydroxyl group proton and the initiator kation; and, since the diol concentration is large as compared with the initiator concentration, there occurs a transfer of active centres into diols which leads the further process.

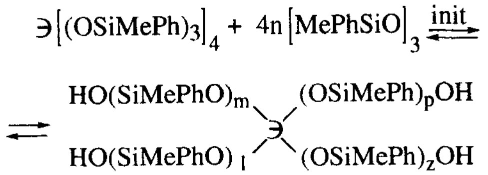
The high rates of proton-kation exchange and the formation of silanolate associates with silanol were proved experimentally in a study of a model system of sodium trimethylsilanoltrimethylsilanolate by the PMR and ^{13}C-NMR spectroscopy [29, 30]. Within this system a rapid exchange reaction of hydroxyl proton to sodium cation goes on:

$$Me_3Si^*OH + Me_3SiONa \rightleftharpoons Me_3Si^*ONa + Me_3SiOH$$

averaging the position of trimethylsilyl signals in the PMR spectrum.

It is that high rate of proton-to-kation exchange reaction that contributes to an active diol entrainment into a reaction with organocyclosiloxanes.

The reactions of polymerization-condensation of cis-1,3,5-methyl-1, 3, 5-triphenylcyclotrisiloxane (cis-A_3) with tetrakis-(3, 5, 7-trimethyl-3, 5, 7-triphenyltrisiloxano-7-hydroxy)-silane (TMPS) and titan (TMPS-Ti) have been studied to obtain polymethylphenylsiloxanes with macromolecules of star-like structure. The reaction were carried out in block at 105°C at the presence of initiator-methylsilanolate of potassium under an argon atmosphere, at the molar ratio of original reagents: cis-A_3 to TMPS-Si/TMPS-Ti = 60:1. This process can be illustrated by the following scheme [31]:



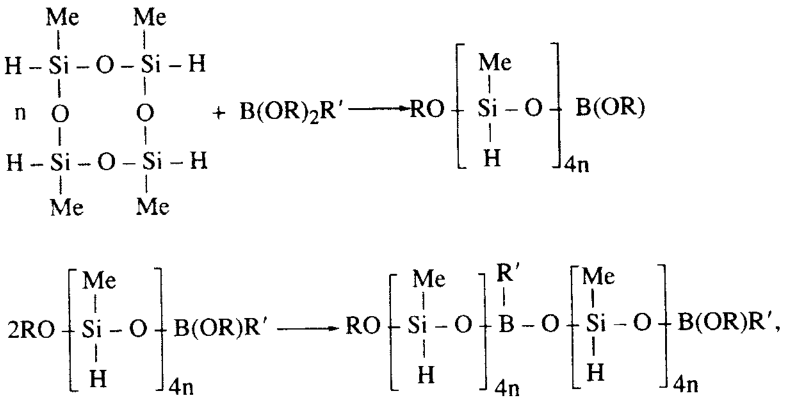
Where ∋ = Si,Ti,
$m + l + p + z = 4n$,
$n = 45 \div 60$.

The distinctive feature of the mentioned reaction is that it proceeds with high velocity. An increase of η_{sp} of the product of CPC occurs in the first 5–10 min of the reaction (the conversion of the cycle reaches ~90% in 10 min) and practically entirely finishes after one hour.

The investigation of hydrodynamical properties as well as the ascertainment of molecular parameters demonstrate, that molecules of the polymer, formed via the reaction between cis-A_3 and TMPS-Si are of tertiaryfunctional star-like structure with one center of branching on a molecule meanwhile the polymer obtained from the reaction of cis-A_3 with TMCS-Ti has number of branching higher than 1. Hence its MM is essentially decreased.

Considering that the partial rearrangement of six-member cycle into eight-member one takes place in the process of anionic polymerization hindering the control on the course of the reaction over the amount of the spending cycle, the process is proposed to be controlled over the change of MM. These investigations substantiated that there is formed the polymer of not high MM during the reaction of cis-A_3 with TMPS-Ti. In a solution its molecules behave as semipermeable clews.

For the reaction of cis-A_3 with TMPS-Ti, the presence of the Ti-atom in the molecule of the latter seems to be of considerable importance due to its ability of being an initiator. The formation of the polymer with not high MM in the case of TMPS-Ti, when the content of the latter is not great, demonstrates that the cutting of chain of the polymer occurs due to spending the Ti- containing component. This discourse can be substantiated by the data from [32], where the reactions of tetramethylcyclotetrasiloxane (D_4^H) with boron acid as well as with its ethers were studied. There is revealed that, at the absence of initiator, the reaction at 135°C in block carries out via the combined polymerization-condensation method in compliance with the scheme:



$$n\,\left[\mathrm{H(Me)Si{-}O{-}Si(Me)H{-}O{-}H(Me)Si{-}O{-}Si(Me)H{-}O}\right]_{\text{cyclo}} + \mathrm{B(OR)_2R'} \longrightarrow \mathrm{RO}\left[\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{Si}}}-\mathrm{O}\right]_{4n}\mathrm{B(OR)}$$

$$2\mathrm{RO}\left[\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{Si}}}-\mathrm{O}\right]_{4n}\mathrm{B(OR)R'} \longrightarrow \mathrm{RO}\left[\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{Si}}}-\mathrm{O}\right]_{4n}\overset{\mathrm{R'}}{\mathrm{B}}-\mathrm{O}\left[\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{Si}}}-\mathrm{O}\right]_{4n}\mathrm{B(OR)R'},$$

where $R = R' = H, C_4H_9$; $R = H, R' = C_6H_5$.

It's evident, that boron acid and its ethers can be considered as initiators.

A detailed study [4, 5] was aimed at the kinetics and mechanism of polymerization polycondensation of methylphenylcyclotrisiloxane (a mixture of cis- and trans-isomers) (A_3) with diethyleneglycol (DEG) in the presence of a nucleophilic initiator – 1,5-dipotassiumoxytrimethyltriphenyltrisiloxane (DPTS). As the kinetics of this reaction showed, both of the reagents react completely under conditions that exclude any possibility of water formation (60°C, in toluene solution), while the rate of consumption of A_3 (up to 70% conversion) is of the first order both in terms of the cycle and the initiator ($W_{A_3} = -K_{A_3}[A_3] \cdot [\mathrm{DPTS}]_0$). Considering the experimental results, the following reaction mechanism was suggested:

$$\sim\!-(\mathrm{SiR_2O})_n\mathrm{K} + \mathrm{HO{-}R'{-}OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \sim\!-(\mathrm{OSiR_2})_n\mathrm{OH} + \mathrm{KO{-}R'{-}OH} \qquad (1)$$

$$\mathrm{HO{-}R'{-}OK} + [\mathrm{R_2SiO}]_3 \xrightarrow{k_2} \mathrm{HO{-}R'{-}(OSiR_2)_3OK} \qquad (2)$$

$$\mathrm{HO{-}R'{-}(OSiR_2)OK} + [\mathrm{R_2SiO}]_3 \xrightarrow{k_3} \mathrm{HO{-}R'{-}(OSiR_2)_{n+3}OK} \qquad (3)$$

$$\mathrm{HO{-}R'{-}OK} + \sim\!-(\mathrm{OSiR_2})_m\sim \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{HO{-}R'{-}OSiR_2{-}(OSiR_2)_{m-n-1}}\sim +$$

$$+\,\mathrm{KO{-}(SiR_2O)_n}\!\sim \qquad (4)$$

Thus, DEG reacts at the expense of a rapid exchange between the diol hydroxyl group proton and the initiator silanolate group kation (stage I), enabling diol to take an active part in the organosiloxane cycle opening reaction.

When this reaction goes on in boiling toluene, it is accompanied by water isolation at the expense of condensation of silanole-groups that form during polymerization polycondensation of A_3 with DEG in the presence of DPTS, an initiator:

$$[\mathrm{R_2SiO}]_n + \mathrm{HO{-}R'{-}OH} \overset{\text{init.}}{\rightleftharpoons} \mathrm{HO{-}R'{-}O{-}(SiR_2O)_n\,H} \qquad (1)$$

$$\sim\!-\mathrm{SiR_2OH} + \mathrm{HO{-}SiR_2O}\!-\!\sim \rightleftharpoons \sim\!-\mathrm{R_2SiOSiR_2O}\!-\!\sim + \mathrm{H_2O} \qquad (2)$$

$$\sim\!-\mathrm{R_2SiOSiR_2O}\!-\!\sim + \mathrm{HO{-}R'{-}OH} \rightleftharpoons \sim\!-\mathrm{R_2SiOR'OH} + \mathrm{HO{-}SiR_2O}\!-\!\sim \qquad (3)$$

$$\sim\!-\mathrm{R_2SiOH} + \mathrm{HOSiR_2}\!-\!\sim \rightleftharpoons \sim\!-\mathrm{R_2SiOSiR_2}\!-\!\sim + \mathrm{H_2O} \qquad (4)$$

$$\sim\!-\mathrm{R_2SiOR'OSiR_2}\!-\!\sim + \mathrm{H_2O} \rightleftharpoons \sim\!-\mathrm{R_2SiOH} + \mathrm{HOR'OSiR_2}\!-\!\sim \qquad (5)$$

According to the above scheme, at the first stage of the reaction, diol reacts with the cycle in the presence of the initiator, forming alkoxysiloxane. The formed end hydroxyl-groups are condensed releasing water and forming new siloxane links (stage 2). At the same time there can proceed a reaction of diol with a linear siloxane chain, yielding alkoxysiloxane and siloxanol (stage 3) which is capable of condensating and forming water (stage 4). The water released in the course of the above described reactions can react over the Si—O—C— link to produce siloxanol and alkoxylosiloxane (stage 5).

The above discussed reaction stages are reversible, and the system's equilibrium, as well as the equilibrium composition will depend significantly on the ratio of the reagents. The role of each reaction will change in the course of the reaction with respect to the reagents ratio and at a constant concentration of the DPTS initiator (10.4×10^{-4} mol/l). Indeed, the rage of water isolation at the initial stage and the amount of water released within the given time interval 10 hours depends significantly on the reagents ratio in the reaction mixture (Fig. 4). It is clear from Figure 4 that maximal conversion (95%) in terms of water released after 10 hours of the reaction, is observed at the cycle-to-diol ratio 6:1 (curve 4); minimal limit conversion in terms of the released water (62%), at 1:1 (curve 5). Meanwhile, as the above scheme evidences, the rate of water formation in relation to the cycle: diol ratio should pass through the maximum. Figure 5 represents the relation of the time required for 30, 50 and 60% conversion of the hydroxyl-group to the molar ratio of A_3 to DEG, showing that the rate of water

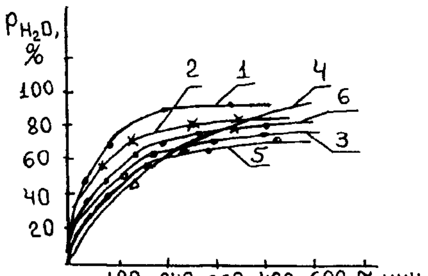


FIGURE 4 H_2O release vs. time of reaction of A_3 and DEG at the A_3-to-DEG: 3:1 (1), 2:1 (2), 5:1 (3), 6:1 (4), 1:1 (5), 1:2 (6).

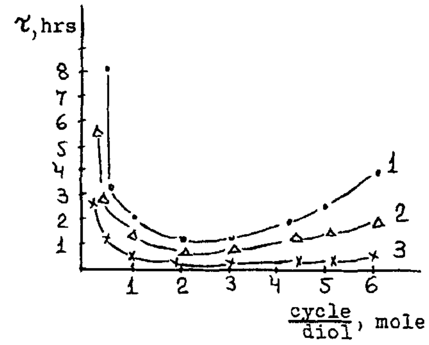


FIGURE 5 The time required to reach the given OH-group concentration in the reaction vs. A_3-to-DEG molar ratio at 30% (1), 50% (2), 60% (3) conversion.

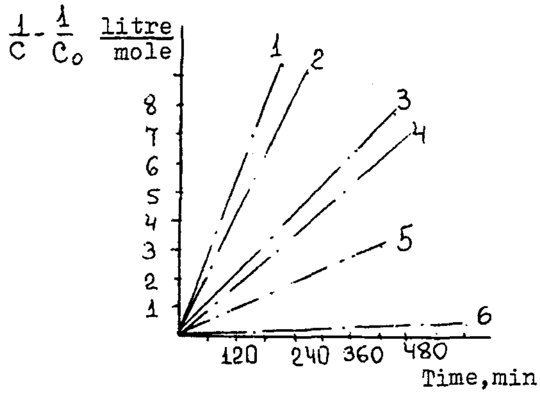


FIGURE 6 $1/C - 1/C_0$ for OH-groups vs. reaction time at the A_3-to-DEG molar ratios: 3:1 (1), 2:1 (2), 5:1 (3), 6:1 (4), 1:1 (5), 1:2 (6).

formation crosses the maximum, with the maximal speed of water isolation at the cycle-to-diol ratio 2:1 – 4.5:1.

A study of the kinetic curves (Fig. 6) shows that in every case at the initial regions of the kinetic curves of the hydroxyl-group conversion to 50–60%, the rate of water release in time is subject to a second order equation and is in linear relation to time.

The obeying of the water release rate relation to the second-order equation is quite understandable considering the equation of water release during silanol-group interaction (stage 2) and alkoxyl and silane-group interaction (stage 5) in the reverse reaction.

Considering the sharp drop of the polymer MM and the reaction rate constant (k_{A_3}) caused by the water concentration increase in the reaction system [33], it appeared interesting to study the kinetics of water release during polymerization polycondensation of various organocyclosiloxanes (A_3, D_4, hexamethylcyclotrisiloxane (D_3) and tetramethyltetravinylcyclotetrasiloxane (D_4^{Vi}) with DEG in the presence of KOH or DPTS [5].

Investigations have proved that the water isolation rate is highly influenced by the cycle stress and the nature of organic substitutes in silicon atom (Fig. 7), the water isolation rate being in all the cases subject to the second-order equation (Fig. 8); the initiator concentration, however, seems to be unimportant (see Fig. 9).

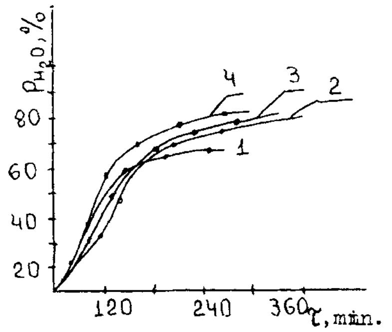


FIGURE 7 H_2O release vs. time in the reaction of DEG with A_s (1), D_4^{Vi}(2), D_4(3), D_3(4) at KON concentration 12×10^{-3} mol/l and at cycle-to-diol molar ratio 1:1.

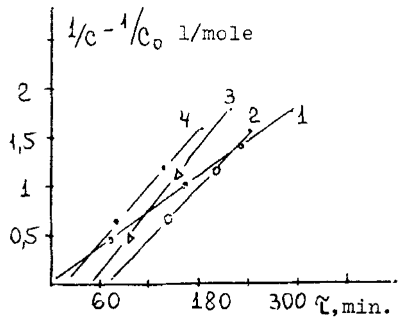


FIGURE 8 $1/C - 1/C_0$ for the OH-groups vs. time of reaction of DEG with D_4^{Vi}(1), D_4(2), A_3(3), D_3(4).

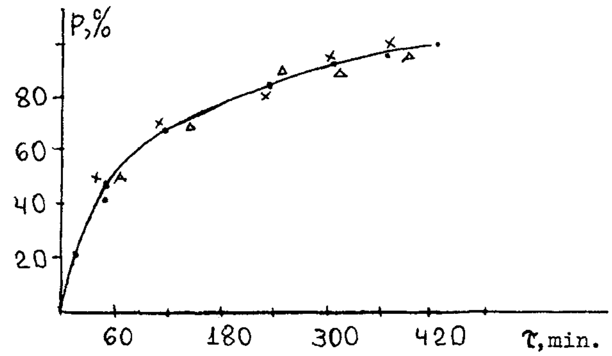


FIGURE 9 H_2O release vs. time of reaction of A_3 with DEG at KON [Me Ph SiO]$_3$K concentration 5.2×10^{-4} (Δ); $10 \times 4 \times 10^{-4}$(·); 52×10^{-4}(0); 104×10^{-4}(x) mol/l.

The polymerization polycondensation reaction of organocyclosiloxanes with α,ω-dihydroxyoligodiorganosiloxanes was used to obtain organosilicon block co-polymers [34]:

$$x \cdot m\,[RR'SiO]_3 + x\,HO\!\left(R''_2SiO\right)_{n}\!H \xrightarrow[-(x-1)H_2O]{\text{init}}$$

$$\longrightarrow HO\left[(RR'SiO)_{3m}\text{—}(R''_2SiO)_n\right]_x H$$

$$RR' = MePh\,,\quad MeVi\,,\quad Me(CF_3CH_2CH_2)\,;\quad R'' = Me$$

The block-copolymers obtained from polymerization polycondensation reaction of organocyclosiloxanes with diols are of a great practical importance in the creation of heat-resistant lubricants, thermoplastic data carriers [35, 36], heat-resistant coating compounds [37, 38]; etc.

Hence, it can be concluded that the combined process of polymerization and polycondensation is at present underlying the formation of macromolecules of quite many polymers with inorganic and organo-inorganic molecular chains. Therefore, speaking in Academician V. V. Korshak's words [39]; when polymers are separated into polymerization and polycondensation ones, one should always take into consideration a considerable conventionality of such separation.

Taking into account, that the sufficiently great number of polymers with organo-inorganic and inorganic macrochains is synthesized by the method of combined polymerization-condensation and the resembling polymers are of long-term to produce non-metallic composites of different purposes one should expect the interest in researching the combined processes of polymerization and polycondensation to increase in the nearest future [40–42].

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