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Catalytic Polymerization of Methylphenyldisilazanes and Alkylphenyl-N-phenylaminosilanes

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Summary

The reaction of polymerization of methylphenyldisilazanes and alkylphenyl-N-phenylaminosilanes under the action of alkalis at high temperature was studied. It was demonstrated that polymerization of the above compounds is accompanied by the evolution of benzene as a result of splitting off of phenyl groups from silicon atoms and of hydrogens from nitrogen atoms. When hydrogen atoms bound with nitrogen were exhausted, in the case of polymerization of symmetrical tetramethylphenyl- and dimethyl-tetraphenyldisilazanes, 1,1,3-trimethyl-1,3,3-triphenyldisilazane, and methyl-diphenylphenylaminosilane, the reaction was kept going by the interaction of phenyls with the protons of the methyl groups. Polymers of a complex structure were obtained as a result.

The literature does not contain any references to the synthesis of polymers out of trialkyl (aryl) aminosilanes or hexaalkyl (aryl) disilazanes. However, such compounds are interesting from the viewpoint of obtaining polymers by a method suggested by one of us (1,2). Dimethylcyclosilazanes and methylphenylcyclosilazanes react under the action of alkalis with the breaking of the Si—C and N—H bonds, ejection of methane (or benzene), and the formation of polymers. It would be logical to assume a similar reaction pattern in the case of polymerization of organodisilazanes and organoaminosilanes.

Earlier (3) we reported an attempt to polymerize hexamethyldisilazane and trimethyltriethyldisilazane under the action of

* N. N. Makarova, graduate student of Moscow Lomonosov Institute of Fine Chemical Technology, took part in the experimental part of the work.

alkali. In the course of the reaction of the aforementioned substances with KOH, we noted the evolution of insignificant quantities of methane and ethane, respectively, but have not succeeded in obtaining polymers, which, it seems, was due to low reaction temperatures. In order to investigate alkaline polymerization of alkyl (aryl) disilazanes and aminosilanes we specially synthesized high-boiling methylphenyldisilazanes of the general formula $[R_x(C_6H_5)_{3-x}Si_2]NH$ and alkylphenyl-N-phenylaminosilanes $RR'C_6H_5SiNHC_6H_5$, where $R = CH_3$ and $R' = CH_3, C_2H_5, C_6H_5$ (4).

It was demonstrated experimentally that under the action of catalytic quantities of KOH at a temperature above 270° on symmetrical tetramethyldiphenyldisilazane, dimethyltetraphenyldisilazane, and 1,1,3-trimethyl-1,3,3-triphenyldisilazane, there occurs a reaction accompanied by the evolution of benzene and formation of polymers. Figure 1 shows the dependence between the evolution of benzene and reaction time. It will be seen that the

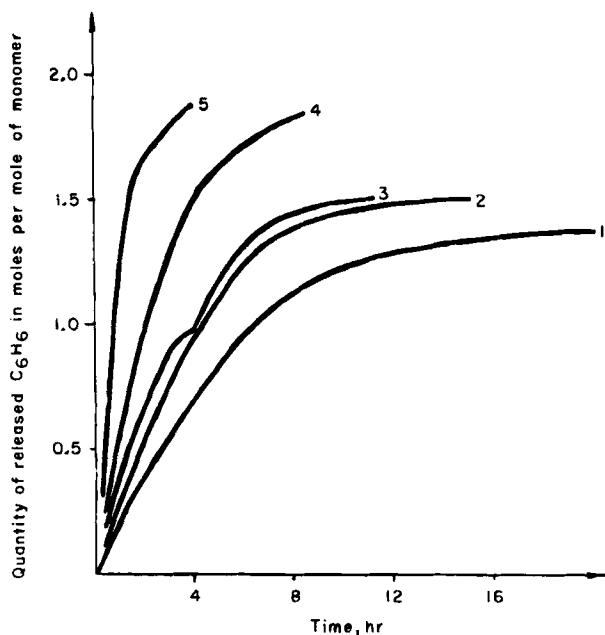


FIG. 1. Polymerization of symmetrical tetramethyldiphenyldisilazane (1,2), 1,1,3-trimethyl-1,3,3-triphenyldisilazane (3), and symmetrical dimethyltetraphenyldisilazane (4,5). Quantity of benzene evolved. Reaction temperature, $^\circ C$: 1, 300 to 320; 2, 310 to 320; 3, 300 to 315; 4, 300; 5, 330 to 340.

quantity of evolving benzene depends not only on the reaction conditions but also on the structure of the initial substance—on the quantity of phenyl groups in the methylphenyldisilazane. In all the noted examples the quantity of benzene is more than 1 mole per mole of initial substance. Therefore, the formation of benzene involves the splitting off of hydrogen, which is not linked with nitrogen because the hydrogen in the nitrogen is exhausted upon the evolution of 1 mole of benzene. In this case the phenyl group which splits from the silicon probably reacts with the hydrogen of the methyl group. As a result of this reaction, benzene is evolved and a Si—CH₂—Si bond appears in the polymer. A comparison of the infrared spectra of the initial monomers and polymers based on them has shown the following: absorption bands typical of N—H groups, 3385 to 3400 cm⁻¹ and 1180 cm⁻¹, disappear from the infrared spectra of the polymers (which points to the participation in the polymerization process of hydrogen bound with nitrogen), and intense absorption bands appear in the 965 and 1030 cm⁻¹ regions, which we explain by the vibrations of the —CH₂— bond (5-7) (see Fig. 2).

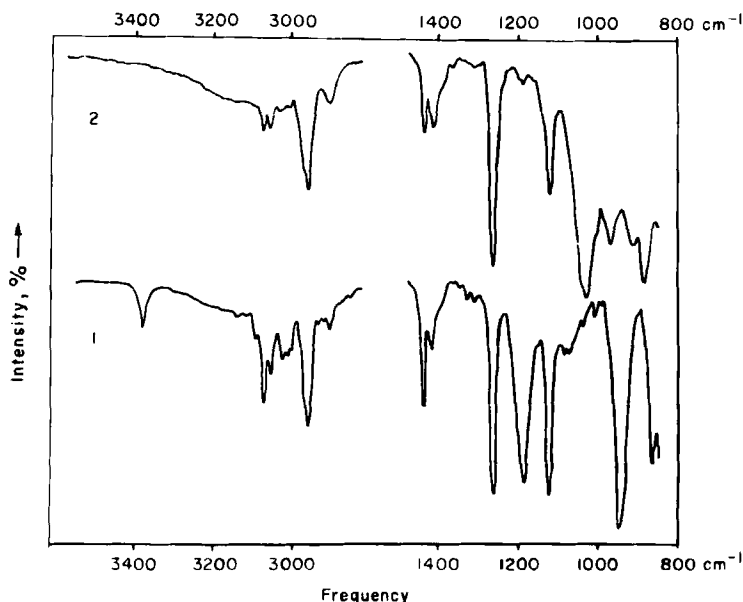
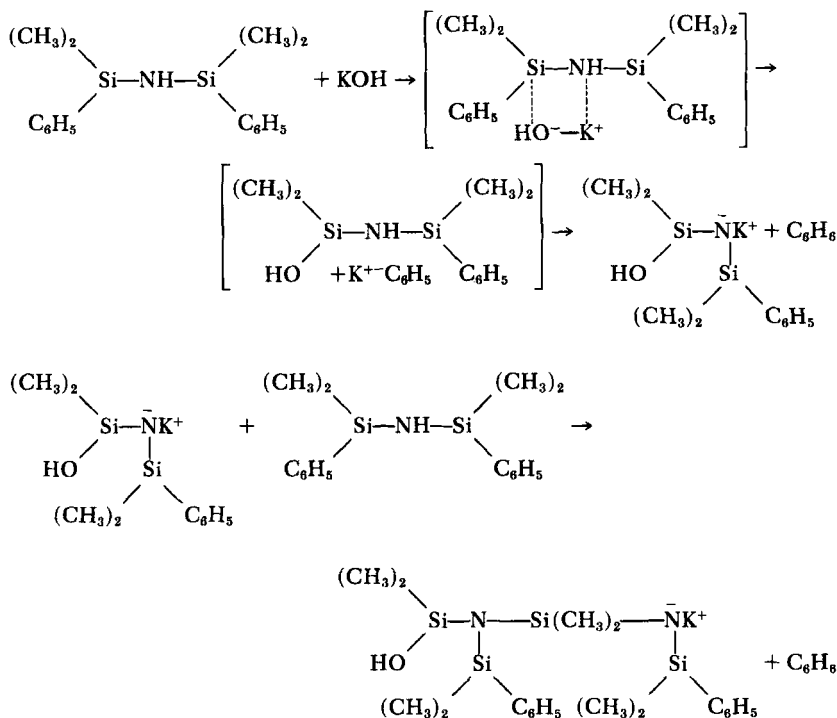


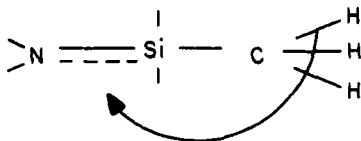
FIG. 2. IR spectra of symmetrical tetramethyldiphenyldisilazane (1) and the polymer-based unit (2).

In the case of tetramethyldiphenyldisilazane, the reaction probably takes the following course:



It should be noted that when the percentage of catalyst was increased (KOH 1.52 wt. %) and upon intense heating (a temperature of 315 to 320° at the beginning of the reaction), we noted that methane is evolved along with benzene.

At the initial stage of the process benzene is evolved, owing to the separation of hydrogen from nitrogen. Polymerization proceeds further through the occurrence of the π - σ conjugation.



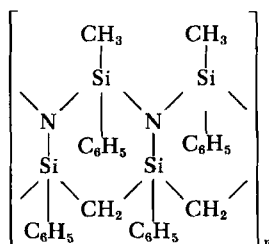
As a result, the mobility of the hydrogen of the methyl group increases and it reacts with the phenylanion. The hydrogen which is linked with nitrogen is more easily protonized than the hydro-

The quantity of benzene evolved as a result of the reaction gives an indication as to the cycles and linear sections of the polymers. As much as 0.5 mole of benzene per mole of organocyclosilazane is evolved as a result of capture by phenyl of protons of the methyl group in the case of polymerization of symmetrical tetramethyl-diphenyldisilazane and 1,1,3-trimethyl-1,3,3-triphenyldisilazane (see Fig. 1), which corresponds to the aforementioned composition at $n \rightarrow 0$. This is also confirmed by polymer analysis (see Table 1).

TABLE I
Properties of Synthesized Polymers

Initial monomer	Catalyst KOH, %	Reaction, temp., °C	Time, hr	Quantity of benzene evolved, moles per mole of monomer	Vitrification temp. of polymer, °C	Molecular weight, M_w/M_n , thousand	Found, %		Calc., %	
							N	Si	N	Si
1. $[(CH_3)_2C_6H_5Si]_2NH$	1.22	300-320	20	1.41	290	300/250	7.84	31.93	8.05	32.3
2. $[(CH_3)_2C_6H_5Si]_2NH$	1.02	310-320	22	1.38	110	21/-	8.13	32.80	7.94	31.9
3. $[CH_3(C_6H_5)_2Si]_2NH$	1.10	320-340	2.75	1.88	220	180/125	8.24	31.96	5.5	22.2
4. $[CH_3(C_6H_5)_2Si]_2NH$	0.94	300	7.5	1.84	160	37/-	8.45	31.56	5.5	22.2

In the case of polymerization of symmetrical dimethyltetraphenyldisilazane as much as 1.9 moles of benzene per mole of initial disilazane is liberated as a result of the reaction. This means that in this case up to 0.9 mole of benzene per each mole of disilazane is evolved as a result of the second reaction. The composition of the polymer is as follows:



Elementary analysis data (see Table 1) and infrared spectra confirm the suggested polymer structure.

Naturally, the suggested patterns of polymer formation do not rule out the possibility of the appearance in the chain of octocyclic

compounds or cycles with a greater or smaller number of atoms, but this is less probable. The polymers obtained as a result of the reaction between symmetrical tetramethyldiphenyl- and dimethyltetraphenyl-disilazanes and KOH are solid brittle substances with a relatively high vitrification temperature, readily soluble in aromatic hydrocarbons, carbon tetrachloride, and other solvents. Thus this reaction does not involve (at least a significant) interaction between the chains, since otherwise insoluble linked products would have been obtained.

The thermomechanical properties of the polymers are shown in Fig. 3. It will be seen from the thermomechanical curves of the

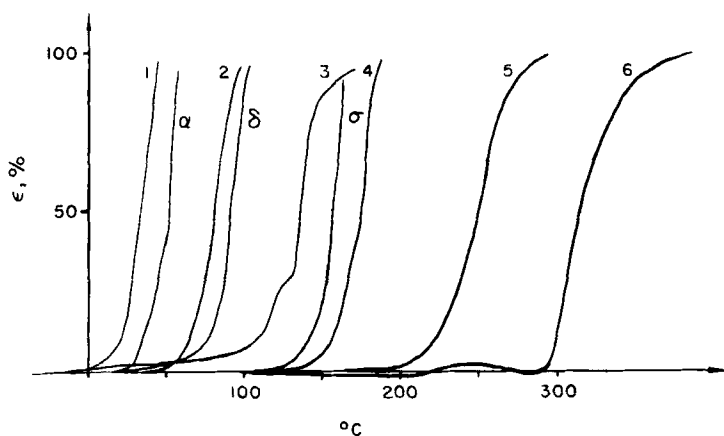
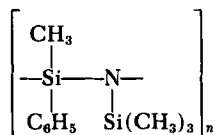


FIG. 3. Thermomechanical curves of polymers. Initial substances: 1 to 3 and 6, *sym*-tetramethyldiphenyldisilazane; 4 and 5, *sym*-dimethyltetraphenyldisilazane; α , δ , and σ , methyl-diphenyl-*N*-phenylaminosilane.

polymers that they behave as typical nonstructural products. Despite the high reaction temperature, the polymers have no region of highly elastic state. This points to the fact that the linear formations between the chain cyclic sections and in the cycles themselves do not exceed the segment value.

An interesting point is that if we polymerize 1,1,1,3-tetramethyl-3,3-diphenyldisilazane, an isomer of symmetrical tetramethyldiphenyldisilazane, the quantity of benzene liberated as a result of the reaction does not exceed 1 mole per mole of the initial monomer, and the resultant polymer is a viscous liquid with a vitrifi-

cation temperature of -50°C , of the following composition:



This means that in the given case the second reaction does not take place.

Investigation of alkaline polymerization reaction on alkylphenylphenylaminosilanes demonstrated its general nature. Dimethylphenyl-N-phenylaminosilane, methylethylphenyl-N-phenylaminosilane, and methyldiphenyl-N-phenylaminosilane react with catalytic quantities of KOH at a temperature above 260° with liberation of benzene, and form compaction products.

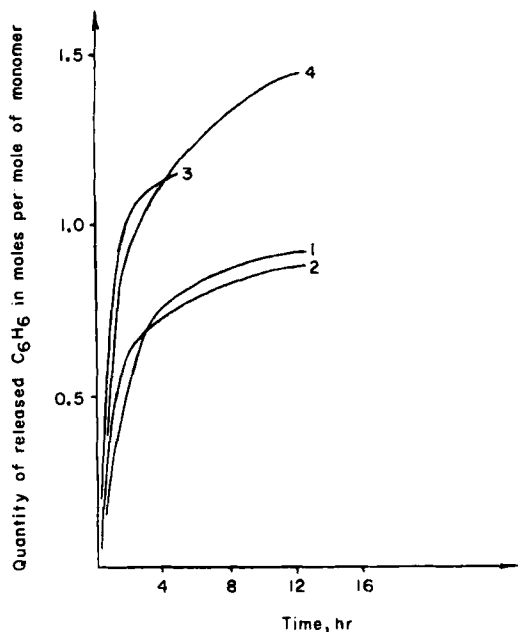
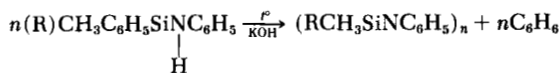


FIG. 4. Polymerization of dimethylphenyl-N-phenylaminosilane (1), methylethylphenyl-N-phenylaminosilane (2) and methyldiphenyl-N-phenylaminosilane (3,4). Quantity of benzene evolved. Reaction temperature, $^{\circ}\text{C}$: 1, 260; 2, 270; 3, 300; 4, 300 to 340. KOH 1%.

The kinetics of benzene evolution is given in Fig. 4. In the case of dimethylphenyl- and methylethylphenyl-N-phenylaminosilanes the reaction runs the following course:



with the formation of low-molecular products mostly of cyclic structure. Polymerization of methyl-diphenyl-N-phenylaminosilane results in the evolution of more than 1 mole of benzene per mole of the monomer, owing to a similar side reaction of splitting off of phenyl groups from silicon atoms and hydrogens from the methyl group. The results are polymers of a complex structure (see Table 2). The thermomechanical properties of certain polymers are shown in Fig. 3.

It is known that the H—N bond is subject to hydrolysis. The ready hydrolysis of the H—N bond in low-molecular compounds is used for analytical purposes (8). With increasing steric hindrances the immunity of the H—N bond to hydrolysis increases. Since the synthesized polymers possess a complex structure they proved to be resistant to acidic, alkaline, and aqueous environments. The results of hydrolysis of different polymers are given in Table 3.

Heating and weight-loss curves were plotted for some polymers. Figure 5 shows the thermogram of a polymer obtained from dimeth-

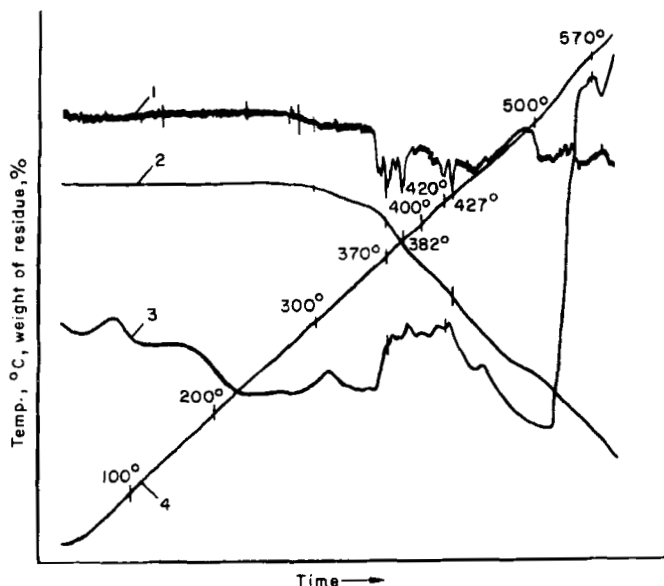
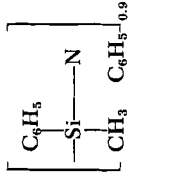



FIG. 5. Thermogram of the polymer obtained from dimethyltetraphenyl-disilazane.

TABLE 2
Quantity of Evolving Benzene; Composition and Properties of Polymers from Methylphenyl-N-phenylaminosilane

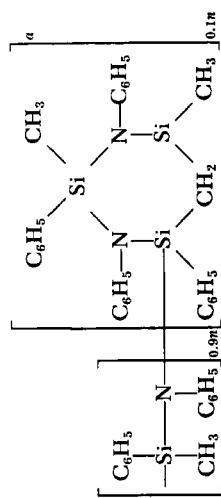
No.	Quantity of benzene evolved, moles per mole of aminosilane	Found, %		Formula	Calc., %		Vitrification temp., °C
		Si	N		Si	N	
1	1.04	13.53	6.65	 $\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---N} \\ \quad \\ \text{CH}_3 \quad \text{C}_6\text{H}_5 \end{array} \right]_{0.9}$ $\left[\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{CH}_3 \\ \quad \\ \text{---Si---N---C}_6\text{H}_5 \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{CH}_3 \end{array} \right]_{0.17}$	13.45	6.72	35
2	1.21	14.51 14.75	6.63 6.70	 $\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---N} \\ \quad \\ \text{CH}_3 \quad \text{C}_6\text{H}_5 \end{array} \right]_{0.3574}$ $\left[\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{CH}_3 \\ \quad \\ \text{---Si---N---C}_6\text{H}_5 \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{CH}_3 \end{array} \right]_{0.6574}$	14.52	7.26	50.57

3	1.25	15.78 15.74	7.10	[]	0.25h	14.70	7.36	75.80
4	1.45	18.02	7.92	[]	0.75h	16.01	7.97	140-150

TABLE 3
Hydrolysis of Polymerization Products

No.	Initial monomer	Polymer	Found		N	%
			Before hydrolysis	After hydrolysis		
1	$[(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}]_2\text{NH}$		8.13°	8.46	8.04	8.39
2	$[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{Si}]_2\text{NH}$		5.23	—	—	4.93

3 $\text{CH}_3(\text{C}_6\text{H}_5)_2\text{SiNHC}_6\text{H}_5$



6.72 6.68 6.65 6.60

^a Hydrolysis time, 15 days.

^b Hydrolysis time, 30 days.

yltetraphenyldisilazane. Curves 1 and 2 show the differential and integral change of polymer weight upon heating at the rate of $3^{\circ}/\text{min}$ in an air stream; curve 3 shows the differential temperature variation. From the polymer heating and weight-loss curves it is evident that the polymer starts losing weight at 300° . Up to 320° the losses are insignificant and are accompanied by the general endothermal effect. Considerable losses in the weight of a sample begin only at 370 to 400° . At this stage of decomposition exothermal effects become predominant. The total weight loss of a sample upon heating to 600° amounted to 45%. Chromatographic analysis of polymer decomposition products in a pyrolytical microreactor has shown that up to 350° benzene is the only decomposition product of the polymer, and that between 350° and 700° a second peak (much smaller in area) appears on the chromatogram. So far we have not been able to identify this peak. Apparently upon further heating of these polymers, condensation occurs.

EXPERIMENTAL

Polymerization was carried out in a three-necked flask with a thermometer, mixer, and Wuertz attachment with a direct condenser, which was followed by a graduated receiving flask for collecting benzene and also a Tishchenko flask with a titrated H_2SO_4 solution. The Tishchenko flask was followed by water-filled cylinders for collecting the gaseous reaction products. Before starting the reaction, the system was blown down with pure nitrogen. The benzene evolved during the reaction was identified by the chromatographic technique. We noted that in prolonged experiments of polymerization of tetramethyldiphenyldisilazane, a small quantity of hexamethyldisiloxane was liberated along with benzene toward the end of the process.

13.99 g of symmetrical tetramethyldiphenyldisilazane and 0.17 g KOH were heated for 20 hr at a temperature of 300 to 320° (gradually raised). During the reaction 5.5 g of benzene and 0.011 g of ammonia were evolved. 6.7 g of a polymer—a solid brittle light-brown substance—were discharged from the flask. The characteristic of the product obtained is given in the first line of Table 1.

30.8 g of symmetrical tetramethyldiphenyldisilazane and 0.47 g of KOH were heated for 15 hr at a temperature of 315 to 320° . Within that time 12.6 g of benzene and 1140 n cm^3 of methane (0.4 mole per mole of initial silazane) were evolved. 16.3 g of a

solid brittle polymer, soluble in benzene, toluene, and acetone, was obtained. Specific viscosity of a 1% solution in toluene was 0.02. Vitrification temperature, 60 to 65°.

Found: 9.16% N; 32.04% Si.

23.4 g of symmetrical dimethyltetraphenylidisilazane and 0.22 g of KOH were heated for 7.5 hr at 300°. Samples of the product were taken periodically during the reaction. 7.95 g of benzene was evolved in the course of the reaction. After the reaction the contents of the flask were vacuumed at a temperature of 260° and 0.34 g of benzene was trapped in a trap cooled with a mixture of dry ice and acetone. 0.002 g of ammonia was trapped in a Tishchenko flask. 11.4 g of a solid brittle polymer (Table 1, line 4) was discharged from the flask.

12.99 g of methylphenyl-N-phenylaminosilane and 0.12 g of KOH were heated for 6 hr at 300°. During the reaction 4.4 g of benzene was evolved. 7.85 g of a solid brittle substance soluble in toluene, benzene, and carbon tetrachloride was discharged. Analysis data are given in Table 2, line 3.

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Zusammenfassung

Die durch Einwirkung von Alkali bei hoher Temperatur erfolgende Polymerisation von Methylphenylidisilazan und Alkylphenyl-N-phenylaminosilan wurde untersucht. Es konnte gezeigt werden, dass die Polymerisation der beiden obigen Verbindungen unter Bildung von Benzol vor sich geht, wobei letzteres durch Abspaltung von an Silicium gebundenen Phenyl-

gruppen und von an Stickstoff gebundenen Wasserstoffatomen entsteht. Wenn die Menge an Stickstoff gebundener Wasserstoffatome erschöpft ist, wird im Falle der Reaktion von symmetrischem Tetramethylphenyl- und Dimethyltetraphenylsilazan, 1,1,3-Trimethyl-1,3,3-triphenylsilazan und Methyl-diphenylphenylaminosilan die Umsetzung dadurch weitergeführt, dass Phenylgruppen mit den Protonen der Methylgruppen reagieren. Polymere mit komplexer Struktur werden als Folge dieser Reaktionen erhalten.

Resumé

La réaction de polymérisation des méthylphényldisilazanes et des alcoylphényl-N-phénylaminosilanes sous l'action des alcalis à haute température a été étudiée. On a montré que la polymérisation de ces composés est accompagnée d'une évolution du benzène, résultant de la scission des groupes phényles des atomes du silicium et des hydrogènes des atomes de l'azote. Lorsque les atomes d'hydrogène liés à l'azote sont épuisés, dans le cas de la polymérisation des tétraméthylphényl- et diméthyltetraphényldisilazanes symétriques, du triméthyl-1,1,3-triphenyl-1,3,3-disilazanes et du méthyl-diphénylphenylaminosilane, la réaction continue par l'interaction des phényles avec les protons des groupes méthyliques. Comme résultat des polymères d'une structure complex sont obtenus.

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