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# Synthesis of the Ladder Polymers by the Reaction of Catalytic Dehydrocondensation

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The heterofunctional condensation of *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane with dimethylchlorosilane has been studied.

It was established that when the reaction proceeds under mild conditions tetraphenylcyclotetrasiloxane incompletely substituted with dimethylsiloxy groups is obtained, i.e., 1,3,5-tris(dimethylsiloxy)-7-hydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane, while under certain conditions 1,3,5,7-tetrakis(dimethylsiloxy)-1,3,5,7-tetraphenylcyclotetrasiloxane is formed.

The catalytic dehydrocondensation of 1,3,5-tris(dimethylsiloxy)-7-hydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane both in a dilute and concentrated solutions in the presence of platinumchlorohydric acid as a catalyst has been studied. It was shown that the reaction proceeds both by the mechanism of intramolecular cyclization with formation of a bicyclic compound and intermolecularly with formation of a tricyclic compound.

The catalytic dehydrocondensation of 1,3,5,7-tetrakis-(hydriddimethylsiloxy)-1,3,5,7-tetraphenylcyclotetrasiloxane with *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane and with oligotetrols ( $m = 5, 10$ ) was also studied. The reaction order, activation energies and dehydrocondensation rate constants were found.

It was established that with an increase in the length ( $m$ ) of the oligotetrols the degree of catalytic dehydrocondensation is reduced. It was shown that if the platinumchlorohydric acid catalyst is replaced by anhydrous powdered caustic potassium a different configuration of the cyclotetrasiloxane skeleton is realized in polymers.

**KEY WORDS** Ladder polymers, dehydrocondensation, tetrasiloxane

## INTRODUCTION

Ladder polyphenylsilsesquioxanes have attracted widespread attention lately.<sup>1–3</sup> It was shown,<sup>4–6</sup> that catalytic dehydrocondensation in the presence of such catalysts as anhydrous caustic potassium, platinumchlorohydric acid and colloid nickel is accompanied by the interaction of  $\equiv\text{Si}-\text{H}$  and  $\equiv\text{Si}-\text{OH}$  with the formation of siloxane bonds.

In References 7 and 8 the authors made an attempt to use the dehydrocondensation of *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane with 1,3,5,7-tetramethylcyclotetrasiloxane in a solution of diethylether, with potassium or sodium methyloxide used as a catalyst. Kinetic investigations of the dehydrocondensation showed that the reaction order is greater than two.

For low levels of transformation, soluble polymers are obtained while at higher conversion the content of the insoluble portion of the polymer increases. Similarly there is an increase in the yield of the insoluble portion of the polymer with an increase in the reaction temperature and the concentration of the solution. This can be explained by the different arrangement of the hydride groups with respect to tetramethylcyclotetrasiloxane plane, which can promote branched system formation.

## EXPERIMENTAL PART

The organic solvents were purified by drying and distillation. The initial *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane and tetrahydroxyphenylsilsequioxanes were synthesized by well-known methods.<sup>9,10</sup>

The IR spectra of all the samples were taken on UR-20 spectrophotometer, while the PMR spectra on a "Perkin-Elmer" R-32 instrument at an operating frequency of 90 MHz in a solution of CCl<sub>4</sub> and dioxane with the internal standard HMDS or TMS.

The purity of the obtained hydridorganocyclosiloxanes was verified on a gas-liquid chromatograph "ΔXM-8M" phase SKTF-100 (10%) on the NAW chromosorb, carrier gas was He, on the 2M column.

Diffractograms were taken on a "ΔPOH-22 instrument, A-Cu<sub>α</sub>, were measured without a filter, the angular velocity of the motor  $\omega = 2$  deg/min.

The thermomechanical curves were taken on a custom-made installation. The test conditions were:  $V = 5$  deg/min,  $\sigma = 0.1$  Kg/cm<sup>2</sup>.

Thermogravimetric investigations were carried out on a "Paulic-Paulic-Erday" derivatograph, model MOM-102. The test conditions were: temperature rate of increase  $V = 5$  deg/min, weight = 100 mg.

*Heterofunctional condensation of cis-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane (tetrol) with dimethylchlorosilane.* To a solution of 13.8 g (0.025 mol) of tetrol in 300 ml of anhydrous toluene at room temperature a solution of 11.4 g (0.12 mol) of the dimethyldichlorosilane was added and the reaction mixture was stirred.

After an hour a solution of 8.68 g (0.1 mol) pyridine in 15 ml of anhydrous toluene was added. The reaction mixture was stirred and heated for 3–4 h until the solvent boiled. The residue was filtered off, the solvent was distilled off, and 15.0 g of a viscous product was obtained, after whose distillation in vacuo, 13.9 g of 1,3,5-tris(hydriddimethylsiloxy)-7-hydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane (1) was isolated,  $T_{\text{boil}} = 190\text{--}192^\circ\text{C}$ ,  $P = 1 \times 10^{-2}$  mmHg, yield 92.6%. The IR bands: 1275 (SiMe); 1000, 1435 (SiPh); 2165 (SiH); 1040, 1080 (SiOSi); 3400–3600 (SiOH).

Calculated for C<sub>30</sub>H<sub>42</sub>Si<sub>7</sub>O<sub>8</sub>, %: C 49.59, H 5.78, Si 26.99, M = 726.

Found: C 49.30, H 5.60, Si 26.75, M = 710.

*Heterofunctional condensation of 1,3,5-tris(hydriddimethylsiloxy)-7-hydroxy-1,3,5,7-*

*tetraphenylcyclotetrasiloxane (I) with dimethylchlorosilane.* To a solution of 13.9 g (0.019 mol) of product (I) in 350 ml of absolute toluene and 15 ml of absolute pyridine at room temperature a solution of 3.6 g (0.038 mol) of dimethylchlorosilane in 15 ml of anhydrous solution was added during 1 h. The reaction mixture was stirred and heated for 4 h until the solvent boiled. The residue was filtered off, the solvent was distilled off, and 13.0 g of viscous product was obtained, after whose distillation in vacuo, 12.0 g of 1,3,5,7-tetrakis(hydriddimethylsiloxy)-1,3,5,7-tetraphenylcyclotetrasiloxane (II) was isolated having  $T_{\text{boil}} = 215\text{--}220^\circ\text{C}$ ,  $P = 1 \times 10^{-2}$  mmHg, yield 92.3%. The IR bands: 1275 (SiMe); 1000, 1435 (SiPh); 2165 (SiH); 1040, 1080 (Si—O—Si).

Calculated for  $\text{C}_{32}\text{H}_{48}\text{Si}_8\text{O}_8$ , %: C 48.98; H 6.12; Si 28.57; M = 784.

Found: C 48.75; H 5.97; Si 28.32; M = 765.

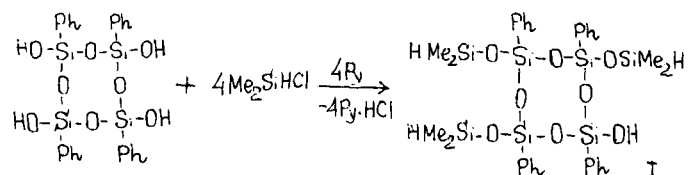
*Dehydrocondensation reaction.* The catalytic dehydrocondensation reaction was carried out in a two-necked flask equipped with a tube for catalyst addition and a reflux condenser with a meter. Between the gasometer and the reflux condenser a cold trap and a wash bottle were installed.

The initial reagents were placed into the flask and dissolved in absolute dioxane and heated in a thermostatted oil bath until a constant temperature was achieved. The catalyst was then introduced, and hydrogen started to be released. Hydrogen was collected in the gasometer. When hydrogen evolution ceased, the solvent was eliminated (if caustic potassium was used as a catalyst, the reaction products were washed to neutral, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ ) and reprecipitated using methanol.

## RESULTS AND DISCUSSION

In the present work, catalytic dehydrocondensation was used to synthesis 1,3,5,7-tetrakis(hydriddimethylsiloxy)-1,3,5,7-tetraphenylcyclotetrasiloxane with tetrol and oligotetrols ladder polyphenylsilsesquioxanes with cis-anti-cis tactic structure of the macromolecules. Polymers of a similar structure were obtained by heterofunctional<sup>11</sup> polycondensation.

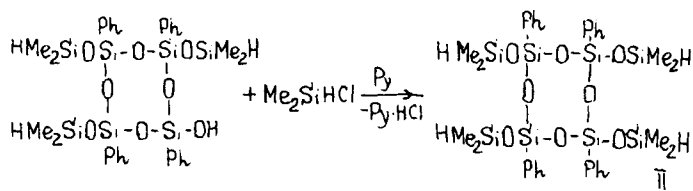
For the purpose of synthesizing tetrakis(hydriddimethylsiloxy)tetraphenylcyclotetrasiloxane, heterofunctional condensation of tetrol with hydridodimethylchlorosilane was carried out using a 1:5 ratio of the initial reagents in an anhydrous solution of diethylether in the presence of pyridine. Despite large excess of hydridodimethylsiloxane, replacement of all four hydroxy groups by hydriddimethylsiloxy groups was not successful. In these conditions only three hydroxy groups are replaced, according to the following scheme:



Incomplete replacement of all four hydroxy groups by hydriddimethylsiloxy groups in these conditions may be explained by the steric effects created by the hydriddimethylsiloxy groups, which is in agreement with Reference 12. The composition and structure of compound 1 were determined by means of functional and elemental analyses, by molecular masses, by IR and by NMR spectra.

In the NMR  $H^1$  spectrum of compound 1, one can observe a singlet signal for methyl protons with a chemical shift  $\sigma = 0.18$  ppm, a complicated multiplet for the phenyl protons in the region 7.0–7.8 ppm. In addition a broadened singlet signal is observed for the Si—H bond in the region of spectrum 2.97–3.15 ppm.

In order to obtain *cis*-1,3,5,7-tetrakis(hydriddimethylsiloxy)-1,3,5,7-tetraphenylcyclotetrasiloxane, the heterofunctional condensation of product 1 with dimethylchlorosilane was carried out in the presence of pyridine. The reaction was run in an anhydrous toluene solution at room temperature. During the final stage the reaction mixture was heated for 3–4 hours until the solvent boiled. Under these conditions the fourth hydroxy group is replaced. HFC proceeds according to the following scheme:



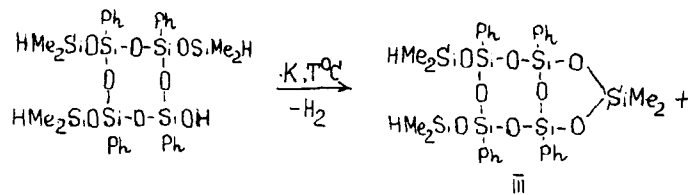
The composition and structure of the synthesized compound II were determined by means of functional and elemental analyses, by molecular mass, by IR and by NMR spectra.

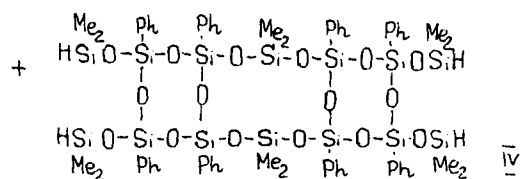
In the NMR  $H^1$  spectrum of compound II one can observe a singlet signal for methyl protons with a chemical shift of  $\sigma = 0.18$  ppm, as well as a complicated multiplet for the phenyl protons in the region 7.0–7.8 ppm and a broadened singlet signal for the Si—H bond in the region 2.97–3.15 ppm. The observed and the calculated values of the phenyl/methyl proton ratio are the same.

In the IR spectrum of compound II the absorption band of the Si—OH bonds disappears and the other absorption bands remain.

Catalytic dehydrocondensation of compound I in a 5% dilute solution of anhydrous toluene in the presence of 0.1 M solution of platinumchlorohydric acid in tetrahydrofuran has also been studied.

The reaction proceeds directly and mainly with the formation of a compound having a bicyclic structure III, whose yield is 83%. Apart from compound III, compound IV, having a tricyclic structure is formed by the following scheme:





The composition and structure of the synthesized compounds III and IV were determined by means of functional and elemental analyses, by molecular mass, by the IR and by NMR spectra (Table I).

In the IR spectrum of compounds III and IV one can observe absorption bands characteristic of asymmetric stretching vibrations of the Si—O—Si bonds in the region 1020 and 1080  $\text{cm}^{-1}$  for compound III and at 1080  $\text{cm}^{-1}$  for compound IV. These are characteristic of the Si—O—Si bond in the cyclotetra- and cyclotrisiloxane rings respectively.

In the NMR spectrum of compound III one can observe a triplet signals for the methyl protons with chemical shifts at  $\sigma = 0.18$  (3H),  $\sigma = 0.32$  (3H) and  $\sigma = 0.44$  (12H) ppm, a complicated multiplet for the phenyl protons in the range of 7.0–7.8 ppm and a broadened singlet signal for the Si—H bond in the range of 2.97–3.15 ppm. For both compounds the observed and calculated values for the ratio of the phenyl and methyl protons is the same.

Catalytic dehydrocondensation was examined at different temperatures (40 and 60°C) in a toluene solution. When the temperature is increased during the catalytic dehydrocondensation, the hydrogen conversion increases from 78% (at 40°C) to 97% (at 60°C) (Figure 1).

Also, the catalytic dehydrocondensation of *cis*-1,3,5,7-tetrakis(hydridimethylsiloxy)-1,3,5,7-tetraphenylcyclotetrasiloxane (II) with tetrol or oligotetrols with a ratio 1:1 has been studied. A 0.1 M solution of platinumchlorhydric acid in tetrahydrofuran or a catalytic quantity of anhydrous powdered caustic potassium was used as the catalyst.

Preliminary heating of the dioxane solution of the initial organocyclosiloxanes (solution concentration  $C = 0.3639$  mole/l) during 6 h in the presence of KOH (0.1% of the total mass of the initial components) and 0.1 M of the platinumchlorhydric acid solution in tetrahydrofuran ( $8 \times 10^{-5}$  g per gram of the substance) in the temperature range of 40–60°C showed that polymerization and polycondensation of the initial cycles does not take place. Detailed analysis of the reaction solution by gas-liquid chromatography showed the absence of water traces and the presence of the initial organocyclosiloxanes. In addition, there are no changes in the NMR spectra of organohydridcyclosiloxanes, and in the IR spectra the absorption bands for the Si—O—Si bonds (for organocyclosiloxanes) are preserved in the range of 1000–1150  $\text{cm}^{-1}$ .

The catalytic dehydrocondensation of compound III with tetrol was examined at 20° and 30°C in absolute dioxane solution in the presence of platinumchlorhydric acid. It was found that under the above conditions the reaction proceeds very slowly. Therefore, the reactions were examined at higher temperatures.

Dehydrocondensation proceeds according to the general scheme:

TABLE I  
Physical and chemical data of organocyclosiloxanes

Ser. N	Yield, %	$T_{\text{bmt}}$ , °C	P, mmHg	M		Calculated, %			Found, %		
				Calc.	Found	C	H	Si	C	H	Si
I	92.6	190–192	0.01–0.02	726	710	49.59	5.78	26.99	49.30	5.60	26.78
II	92.3	215–220	0.01–0.02	784	765	48.98	6.12	28.57	48.75	5.97	28.32
III	83.0	190–191	0.01–0.02	7724	7000	49.72	5.52	27.07	49.32	5.34	26.88
IV	12.4	290–297	0.01–0.02	1448	1410	49.72	5.52	27.07	49.45	5.37	26.96

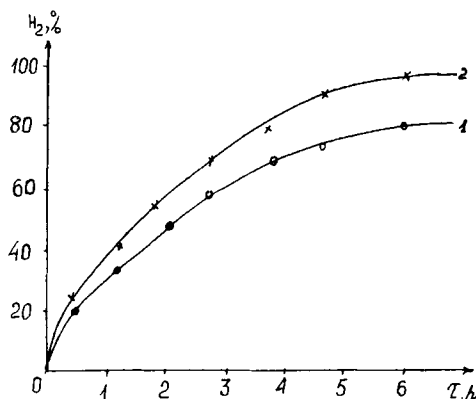
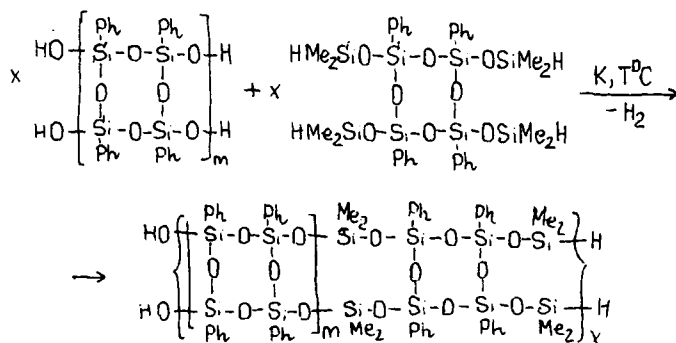


FIGURE 1 Hydrogen conversion in the reaction of dehydrocondensation of 1,3,5-tris(hydriddimethylsiloxy)-7-hydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane in the presence of platinumchlorohydric acid: curve 1 corresponds to a reaction temperature of 40°C, curve 2 at 60°C. ( $C = 0.3639$  mole/l).

TABLE II  
Physical and chemical data of polymers

Ser. N	Yield, %	$\eta$ spec. 1% Toluene solution 25°C	$T_{melt}$ °C	$d_1$ , Å	$d_2$ , Å
V	80	0.07	123-130	—	—
V'	86	0.09	127-135	—	—
V''	94	0.12	140-145	11.65	4.48
V'''	91	0.10	126-132	—	—
VI	78	0.10	175-181	12.03	4.48
VII	70	0.08	161-170	—	—



where:

$m = 1$  - V(40°C), V'(50°C), V''(60°C), ( $\text{H}_2\text{PtCl}_6$ ), V'''(50°C, KOH).

$m = 5$  - VI(60°C);  $m = 10$  - VII(60°C), ( $\text{H}_2\text{PtCl}_6$ ).

The reaction products are hard transparent polymers, soluble in organic solvents. Table II shows the results of the elemental analysis of the physical/chemical properties and the yields of the synthesized polymers.



It was observed that for temperature increases during the dehydrocondensation reaction of compound II with tetrol the hydrogen conversion increases from 83% (40°C) to 97% (60°C), in case when platinochlorohydric acid was used as catalyst (Figure 2). In the case when powdered potassium hydroxide was used to catalyze the dehydrocondensation reaction, it proceeds more vigorously (Figure 2, curve 3).

When examining the catalytic dehydrocondensation reaction of compound II with tetrol in the presence of platinochlorohydric acid, the reaction order, rate constant and activation energy were determined. It appeared that the catalytic dehydrocondensation reaction is of the second order. Figure 3 shows the hydrogen release rate in the reaction of catalytic dehydrocondensation of compound II with oligotetrols ( $m = 5.10$ ) at 60°C. As is seen from Figure 3 with an increase in the length of the oligotetrols  $m$ , the rate and the degree of catalytic dehydrocondensation decreases.

Figure 4 shows the direct dependence of the inverse concentration of the reactants

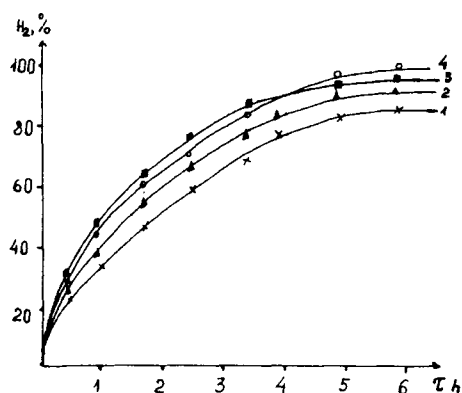


FIGURE 2 Hydrogen conversion in the dehydrocondensation of 1,3,5,7-tetrakis(hydriddimethylsiloxy)-1,3,5,7-tetraphenylcyclotetrasiloxane with tetrol: curve 1 corresponds to a reaction temperature of 40°C, curve 2 = 50°C, curve 4 = 60°C in the presence of platinochlorohydric acid. Curve 3 corresponds to a reaction temperature of 50°C in the presence of KOH.

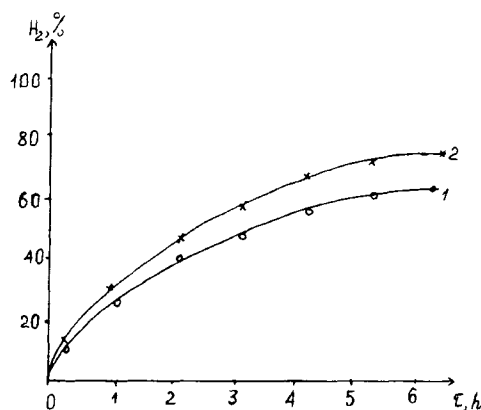


FIGURE 3 Hydrogen conversion in the catalytic dehydrocondensation of 1,3,5,7-tetrakis(hydriddimethylsiloxy)-1,3,5,7-tetraphenylcyclotetrasiloxane with oligotetrols ( $m = 5.10$ ) at 60°C: curve 1 corresponds to oligotetrol  $m = 10$ , curve 2 to oligotetrol  $m = 5$ .

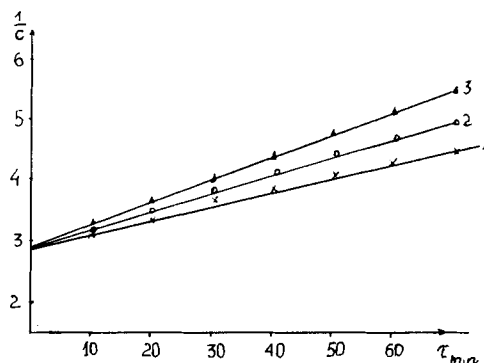


FIGURE 4 Time dependence of inverse concentration of the reagents during the catalytic dehydrocondensation: curve 1 corresponds to a reaction temperature of 40°C, curve 2 = 50°C, curve 3 = 60°C.

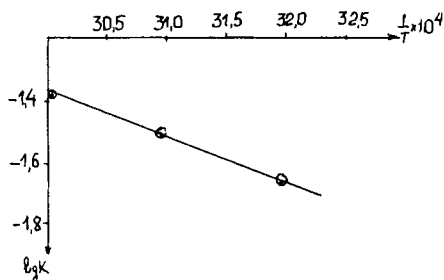
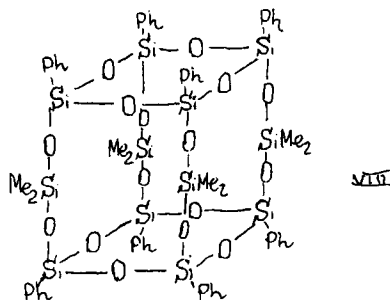


FIGURE 5 Dependence of the reaction rate constant logarithm on the inverse temperature.

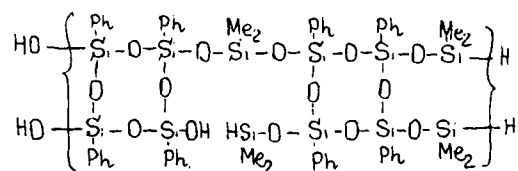
on time. The reaction rates at various temperatures were calculated:  $K_{40^{\circ}\text{C}} = 2.22 \times 10^{-2}$ ;  $K_{50^{\circ}\text{C}} = 3.15 \times 10^{-2}$ ;  $K_{60^{\circ}\text{C}} = 4.14 \times 10^{-2}$ . It was found that for each increase in the temperature of 10°C, the reaction rate constants increase approximately 1.4 times.

Figure 5 shows the dependence of the reaction rate logarithm on inverse temperature, from which the activation energy of the catalytic dehydrocondensation reaction was calculated:  $E_{\text{activ.}} = 29.4 \text{ KJ/mol}$ .

It should be noted that in the case of catalytic dehydrocondensation, it is unlikely that the reaction proceeds by the mechanism of intramolecular cyclization with formation of a compound of structure VIII:



Besides, in a ladder polymeric chain defect structures can exist:



which may only be formed as a result of an incomplete catalytic dehydrocondensation. The existence of defect structures increases the flexibility of the polymeric chain and decreases the softening temperature. With temperature increases in the

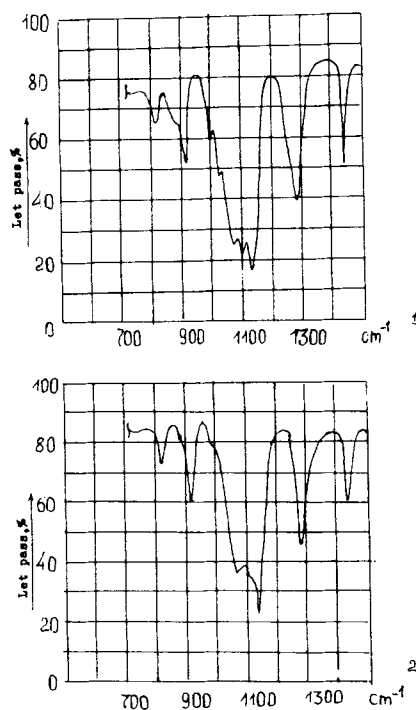


FIGURE 6 IR spectra of polymers: curve 1 for polymer V'', curve 2 = V'''.

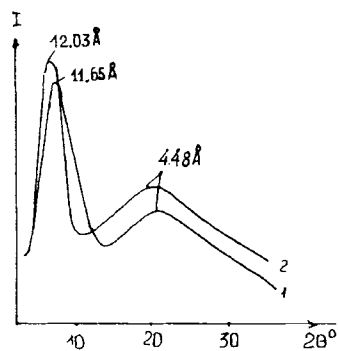


FIGURE 7 Diffractograms of polymers: curve 1 corresponds to polymer V'', curve 2 = VI.

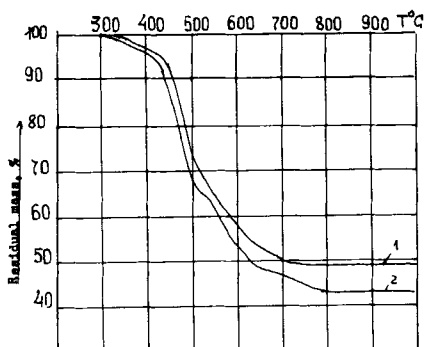


FIGURE 8 The thermogravimetric curves of the polymers: curve 1 corresponds to polymer V'', curve 2 = VI (in air, the temperature increase rate of 5 deg/min).

catalytic dehydrocondensation reaction the amount of defect structures decreases, which leads to an increase in the softening temperature and to an increase in the molecular weight.

In the IR spectra of the synthesized polymers one can observe absorption bands characteristic of asymmetric valence oscillations of the Si—O—Si bond in the region of  $1000\text{--}1200\text{ cm}^{-1}$ , peculiar to the absorption bands of Si—O—Si bonds at 1040, 1070, 1100 and  $1130\text{ cm}^{-1}$  for the polymers obtained in the presence of platinum-chlorohydric acid, while in the IR spectra of the polymers obtained in the presence of powdered potassium hydroxide absorption bands for asymmetric valence oscillations for the Si—O—Si bonds at  $1100\text{ cm}^{-1}$  disappear and the absorption bands at 1070 and  $1130\text{ cm}^{-1}$  remain. This implies that in the presence of catalytic amounts of powdered potassium hydroxide the catalytic regrouping of the cyclotetrasiloxane skeleton with the formation of another macromolecular chain structure occurs (Figure 6).

The synthesized polymers were analyzed by an x-ray method. As is seen from the amorphous polymer diffractogram (Figure 7) for polymer V'' and VI one can observe two diffraction maximums, at  $d_1 = 11.65\text{ \AA}$  and  $d_2 = 12.03\text{ \AA}$ , respectively, indicating the interchain distance in the synthesized polymers. This value of  $d_1$  is close to the interchain distance for polyorganosilsesquioxanes.<sup>11</sup> The value of  $d_2$  is more complicated and characterizes both interchain and interatomic distances.

It was shown by thermogravimetric investigations (Figure 8), that the polymers have a higher thermal-oxidative stability. For polymers V'' and VI at  $400^\circ\text{C}$  mass losses do not exceed 3–6%; and the main destruction process proceeds in the range  $450\text{--}650^\circ\text{C}$ . Above  $700^\circ\text{C}$  the curves for mass loss do not change.

Thus, we have for the first time shown the possibility of obtaining ladder polyorganosilsesquioxanes soluble in organic solvents, by the catalytic dehydrocondensation of 1,3,5,7-tetrakis-(hydriddimethylsiloxy) = 1,3,5,7-tetraphenylcyclotetrasiloxane with tetroxol and oligotetroxols.

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