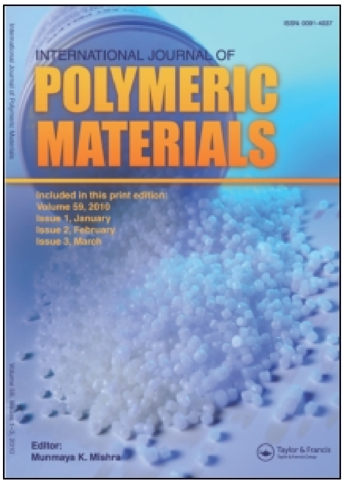

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Organosilicon Polycyclic Copolymers of Bead-like Structure

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The reaction of catalytic dehydrocondensation of dihydroorganocyclotetra(hexa)siloxanes with dihydroxyorganocyclotetra(hexa)siloxanes in the presence of platinochlorohydric acid of anhydrous powder-like caustic potassium has been studied.

High-molecular organosilicon polycyclic copolymers of the bead-like structure with cyclotetra- and cyclohexasiloxane fragments in the chain completely dissoluble in organic solvents were synthesized.

Reaction order, activation energies and dehydrocondensation rate constants were found. Thermogravimetric, thermomechanical and X-ray studies of the synthesized polymers were carried out.

KEY WORDS Organosilicons, polycyclic, bead-like structures.

INTRODUCTION

It is known[1] that compounds with the Si—H bond interact with water with elimination of hydrogen in the presence of alkali catalysts:

$$\equiv\text{Si—H} + H_2O \rightarrow \equiv\text{Si—OH} + H_2$$

The reaction of catalytic dehydrocondensation between $\equiv$Si—H containing compounds and hydroxyl-containing organic compounds[2,3] proceeds similarly. In the above mentioned transformations the reaction capacity of the $\equiv$Si—H bond is determined by catalyst nature and amount, temperature, reactant concentration, solvent character, etc.[3,4]

In the reactions of catalytic dehydrocondensation of organohydroxysilanes with organohydroxysilanes such catalysts were used as colloid nickel, anhydrous zinc chloride, platinochlorohydric acid[5,6] with which the process runs according to the scheme:

$$\equiv\text{Si—H} + \text{HO—Si}\equiv \xrightarrow[-H_2O]{} \equiv\text{Si—O—Si}\equiv$$

The authors of References 7–9 for the first time studied the reaction of catalytic dehydrocondensation of hydrid-containing organosiloxanes with hydroxy-containing organosilanes and siloxanes in the presence of powder-like caustic potassium as nucleophilic catalyst, and as in References 10 and 11, they showed that under the action of the nucleophilic catalysts the competing reaction of dialkylsiloxane elimination does not take place, which is explained by a high rate of the dehydrocondensation process.

Besides, it was shown[8,9] that replacement of KOH with alcoholate or trimethylsilanolate of potassium does not exert a substantial effect on the process, and hence KOH was preferred.

By catalytic dehydrocondensation of linear α, ω-dihydroxydiorganosiloxanes with α, ω-dihydroxydiorganosiloxane in the presence of caustic potassium, depending on the length of the siloxane fragment, both individual organosiloxanes and linear copolymers were synthesized.[12]

In the literature there is practically no information on the reaction of catalytic dehydrocondensation of hydrid-containing organocyclosiloxanes with hydroxyl-containing organocyclosiloxanes. Only in Reference 13 this reaction between tetramethylcyclotetrasiloxanes and cis-1,3,5,7-tetrahydroxytetraphenylcyclosiloxanes in the presence of potassium or sodium methylate was studied, and it was established that with an increase of hydrogen conversion the content of insoluble polymer increases.

EXPERIMENTAL

The purity of all the initial organochlorosilanes was controlled by their boiling temperatures, Cl ions content and refraction indices.

The organic solvents were cleaned by drying and distillation.

The initial hydrid- and dihydroxyorganocyclotetra(hexa)siloxanes were synthesized by well-known methods.[14-16]

The IR spectra of all the samples were taken on an UR-20 instrument, while the PMR spectra—on a "Perkin Elmer" R-32 instrument at an operating frequency of 90 MHz in the solutions of CCl_4 and dioxane with internal ethanol of HMDS or TMS.

The purity of the obtained organocyclosiloxanes was verified on a gas-liquid chromatograph "CVET-4" or "LMH-8MD" phase SRTP-100 (10%) on the NaW chromosorb, carrier gas was He, on the column 2M.

Diffractograms were taken on a "DRON-2" instrument. A-Cu were measured without a filter, the angular velocity of the meter = 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^2.

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

Heterofunction Condensation of Methyldichlorosilane with 1,3-Dihydroxytetraphenyldisiloxane

To the solution of 11.5 g (0.1 mol) methyldichlorosilane in 250 ml of anhydrous toluene at room temperature 47.4 g (0.7 mol) of 1,3-dihydroxytetraphenyldisiloxane in 400 ml of anhydrous toluene was poured. The reaction mixture was stirred and heated up for 3–4 h until the solvent boiled. The residue was filtered off, the solvent was driven off, and 56.3 g of viscous product was obtained, after whose distillation in vacuo, 20 g of 1-hydrid-1-methyltriphenylcyclotrisiloxane (I) was isolated having $T_{\text{boil}} = 190–195°C$, $P = 1 \times 10^{-2}$ mmHg, yield: 36%

The IR bands: 1275 (SiMe); 1435 (SiPh); 1020 (SiOSi); 2170 (SiH).

Calculated for $C_{25}H_{24}Si_3O_3$:	C 65.79	H 5.26	Si 18.42	M=456
Found:	C 65.10	H 4.99	Si 18.30	M=432

23.6 g of 1.7-dihydrid-1,7-dimethyloctaphenylcyclohexasiloxane(II) with $T_{\text{boil}} = 263–267°C$, $P = 1 \times 10^{-2}$ mmHg, $T_{\text{melt}} = 162–163°C$ (after recrystallization from hexane), yield: 42%.

The IR bands: 1275 (SiMe); 1435 (SiPh); 1060 (SiOSi), 2170 (SiH).

Calculated for $C_{50}H_{48}Si_6O_6$:	C 65.79	H 5.26	Si 18.42	M=912
Found:	C 66.08	H 5.38	Si 18.11	M=891

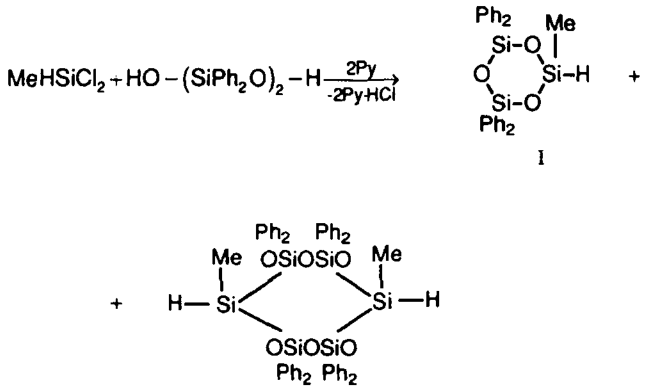
Dehydrocondensation reaction. Catalytic dehydrocondensation reaction was carried put in a two-necked flask equipped with a tube for catalyst inlet, reflux condenser connected with a gasometer. Between the gasometer and reflux condenser a cold trap and a wash bottle were installed.

The reaction products were placed into the flask and thermostatted in an oil bath until constant temperature was set up. Then the catalyst was introduced. After that hydrogen started to release. Hydrogen was collected in the gasometer. Hydrogen having ceased releasing, the reaction mixture was heated up to 60–80°C for 3–4 h, after which the solvent was eliminated (if caustic potassium was used as a catalyst, the reaction products were washed to neutral medium).

RESULTS AND DISCUSSION

In the present work, by means of catalytic dehydrocondensation of hydridoorganocyclosiloxanes with hydroquiorganocyclosiloxanes, polycyclic copolymers of the bead-like structure have been synthesized. The copolymers of a similar structure were obtained by us earlier in the reactions of homo-[17] and heterofunctional[18] polycondensation.

1,7-dihydrid-1,7-dimethyloctaphenylcyclohexasiloxane(compound II) was obtained in the reaction of heterofunctional condensation of methyldichlorosilane with a 1:1 ratio of the initial components in the presence of pyridine and at 20–25°C, according to the following Scheme:



I

II

The composition and structure of the synthesized compounds were determined by means of functional and elementary analyses, by finding molecular masses by IR and NMR spectra.

In the NMR spectrum of compound II one can observe two singlet signals for the Si—Me group with chemical shift in the region of 0.26 and 0.30 ppm, characterizing cis- and trans-isomers. Besides, in the spectrum a singlet signal is observed for the Si—H bond in the region 2.78 ppm.

It is known[19] that if platinochlorohydric acid is used as a catalyst, the hydrogen conversion is not high, but the authors of Reference 6 showed that upon utilization of the same polyaddition catalyst in the dehydrocondensation reactions, hydrogen conversion in some cases is quantitative.

Taking into account this fact when studying the dehydrocondensation reaction, we used platinochlorohydric acid. Besides, we used catalytic quantity of anhydrous powder-like caustic potassium as a catalyst.

Preliminary heating of the initial organocyclosiloxanes during 4 h in the presence of KOH (0.1% of the total mass of the initial components) and 0.1 M of the platinochlorohydric acid solution in tetrahydrofuran ($\sim 5 \times 40^{-4}$ g per gram of a substance) in the temperature range 40–50°C showed that polymerization of the initial cycles does not take place. Besides, there are no changes in the PMR spectra of organocyclosiloxanes for methyl protons.

In case of using platinochlorohydric acid, the catalytic dehydrocondensation reaction proceeds rather vigorously. It should be noted, however, that at the initial stages of dehydrocondensation one can observe an induction period (~1–2 min).

The reaction of catalytic dehydrocondensation was examined at different temperatures (+20, +30 and +40°C) in the solution of absolute toluene. When the dehydrocondensation reaction in the solution was conducted with anhydrous KOH as a catalyst, the hydrogen conversion increased from 10 to 50%.[6] In our case with temperature rise in the reaction of catalytic dehydrocondensation the hydrogen conversion increases from 66% (at 20°C) to 82% (at 40°C) (Figure 1).

In order to increase the depth of catalytic dehydrocondensation (in case of platinochlorohydric acid is used as a catalyst), at the final stage the reaction was heated up to 80°C for 3–4 h.

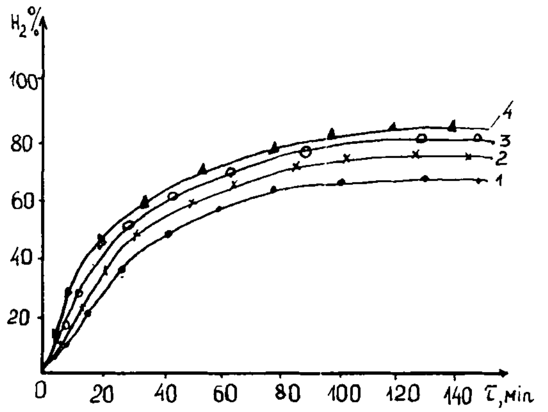
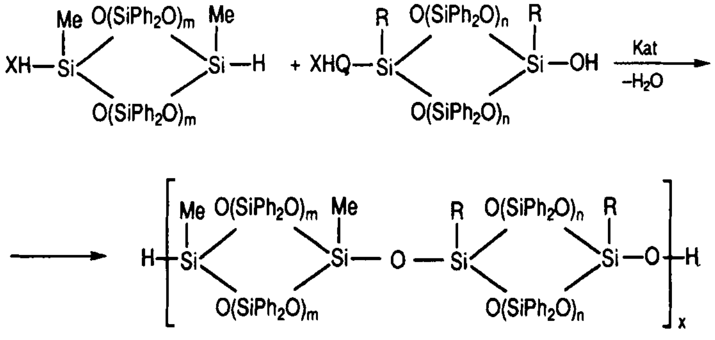


FIGURE 1 Hydrogen release rate in the reaction of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,5-dihydroxy-1,5-dimethyltetraphenylcyclotetrasiloxane, where curve 1 is at 20°C, curve 2 is at 30°C, curve 3 is at 40°C in case of dehydrocondensation of 1,5-dihydroxy-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,5-dihydroxyhexaphenylcyclotetrasiloxane.

Dehydrocondensation proceeds according to the general Scheme:

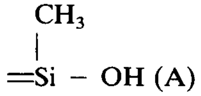


where:

m = 1, n = 1, R = Me(I); m = 1, n = 1, R = Ph(II);
m = 1, n = 2, R = Me(III); m = 2, n = 2, R = Ph(IV);
m = 2, n = 1, R = Ph(V); m = 1, n = 2, R = Ph(VI).

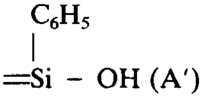
It is known that apart from the catalyst nature and amount, temperature, nature of solvent, etc., a strong influence on the reaction capacity of the Si—H bond is exerted by steric and inductive effects caused by surrounding groups in silicon.

When considering the fragments



$$\overset{\displaystyle CH_3}{\underset{|}{}}\;\; {=}Si - OH \;(A)$$

and



$$\overset{\displaystyle C_6H_5}{\underset{|}{}}\;\; {=}Si - OH \;(A')$$

one can see that the methyl group will increase silicon electronegativity. Hence, the proton of the hydroxyl group in fragment A will be less electropositive, than that in fragment A′.

$$G_{A}^{H(OH)} > G_{A'}^{H(OH)}$$

and, consequently, the interaction of the compounds containing fragment A with dehydridcyclosiloxanes must be inhibited, but, on the other hand, in fragment A′, due to the steric effect of the phenyl surrounding groups, the reaction capacity of hydroxyl groups must be decreased, i.e.

$$S_{A}^{H(OH)} < S_{A'}^{H(OH)}$$

Therefore, the net effect G of the methyl and phenyl substituents in the reactions under investigation is approximately the same (Figure 1, curves 3, 4):

$$G_{A}^{H(OH)} \simeq G_{A'}^{H(OH)}$$

It should be noted that at catalytic dehydrocondensation of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,7-dihydroxyoctaphenylcyclohexasiloxane (Figure 2), the hydrogen conversion (at 40°C, H_2PtCl_6) is 69%, which can be explained by an increase in rigidity of the polymer chain and enhancement of the steric effect.

When examining the catalytic dehydrocondensation reaction of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane 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 a direct dependence of the reverse concentration of the reactants

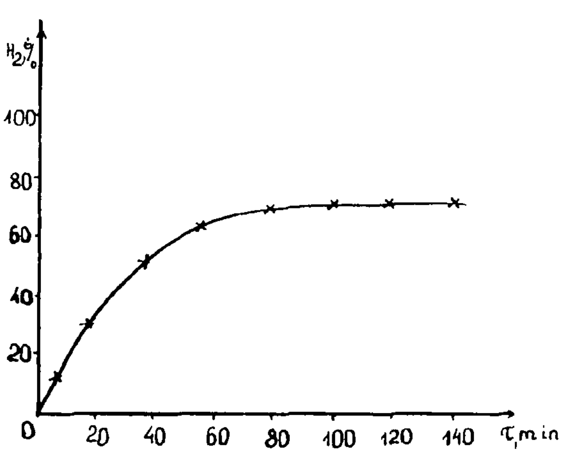


FIGURE 2 Hydrogen release rate at dehydrocondensation of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,7-dihydroxyoctaphenylcyclohexasiloxane at 40°C in the presence of H_2PtCl_6.

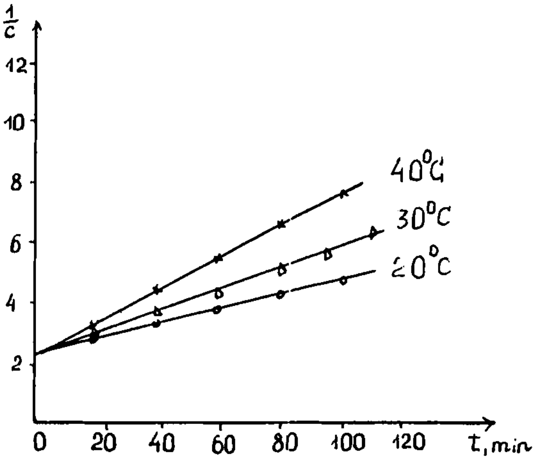


FIGURE 3 Time dependence of the reverse concentration of the reactants (c = 0.44 mol/l, catalyst being H_2PtCl_6).

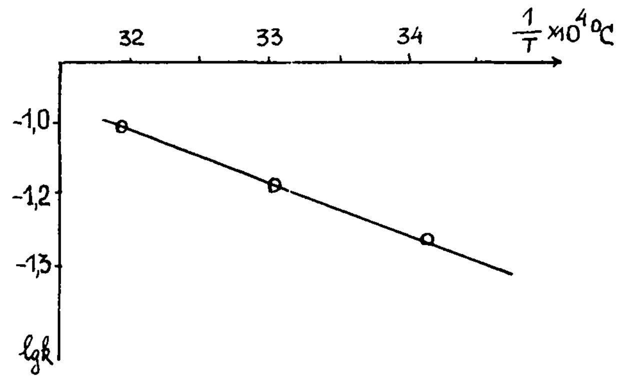


FIGURE 4 Dependence of the reaction rate logarithm on reverse temperature (catalyst being H_2PtCl_6).

on time. The reaction rates at various temperatures were calculated: $K_{20°C} = 5.17 \times 10^{-2}$; $K_{30°C} = 7.47 \times 10^{-2}$; $K_{40°C} = 10.86x \times 10^{-2}$.

Figure 4 shows the dependence of reaction rate logarithm on temperature, from which the activation energy of the catalytic dehydrocondensation reaction was calculated: 28 kJ/mol.

Similarly, we have investigated the catalytic dehydrocondensation reactions in the presence of powder-like KOH in absolute toluene. In the course of the reaction the hydrogen conversion was examined in time (Figure 5).

In the case of the catalytic dehydrocondensation reaction of 1,5-dehydrid-1,5-dimethyltetraphenylcyclotetrasiloxane in the presence of KOH, it was determined that the given reaction is of the second order. Figure 6 shows the dependence of the reverse concentration on time; the reaction rate constants are: $K_{20°C} = 6.9 \times 10^{-2}$; $K_{30°C} = 9.75 \times 10^{-2}$ and $K_{40°C} = 14 \times 10^{-2}$.

Figure 7 shows the dependence of the reaction rate logarithm on temperature, from which the activation energy was calculated Σ_{act} = 28.1 kJ/mol. Therefore, in the case of using both catalysts, the activation energy is the same.

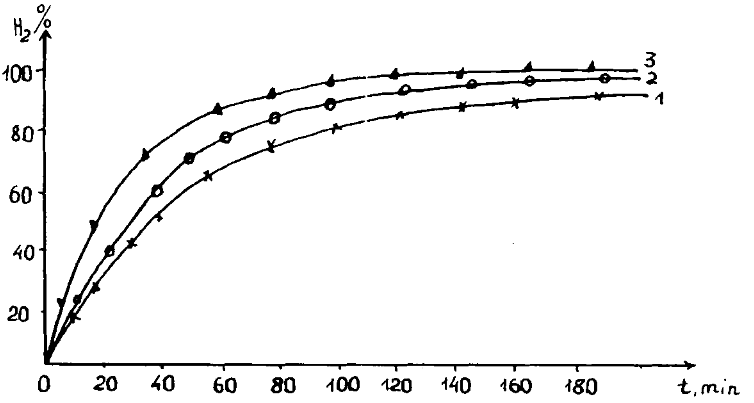


FIGURE 5 Hydrogen release rate in the reaction of dehydrocondensation of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,5-dihydroxy-1,5-dimethyltetraphenylcyclotetrasiloxane; curve 1 is at 20°C, curve 2 is at 30°C, curve 3 is at 40°C (catalyst being KOH).

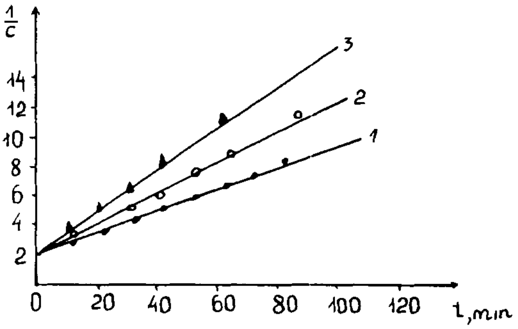


FIGURE 6 Time dependence of the reverse concentration of the reactants upon dehydrocondensation of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,5-dihydroxy-1,5-dimethyltetraphenylcyclotetrasiloxane (c = 0.44 mol/l, catalyst being KOH), where curve 1 is at 20°C, curve 2 is at 30°C, curve 3 is at 40°C.

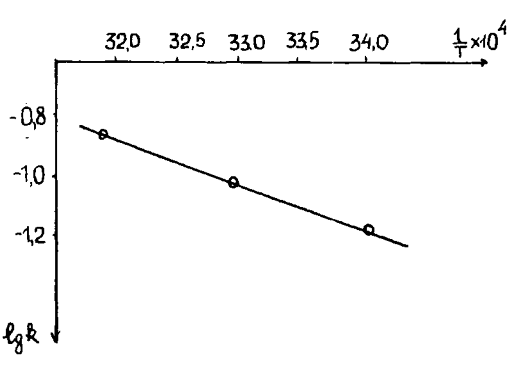


FIGURE 7 Dependence of the reaction rate logarithm on reverse temperature (catalyst being KOH).

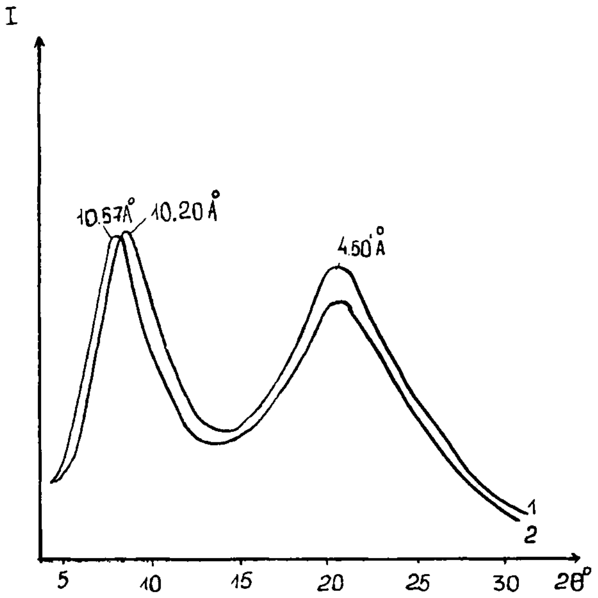


FIGURE 8 Diffractograms of copolymers, where curve 1 is for copolymer III, curve 2 is for copolymer VI.

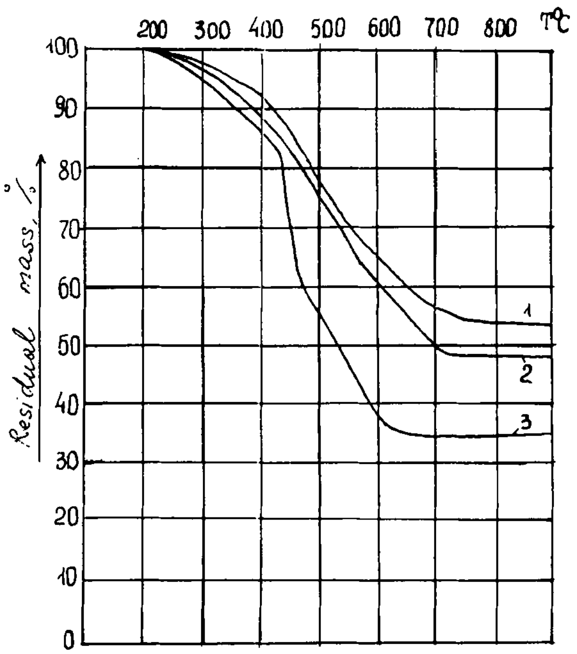


FIGURE 9 The thermogravimentric curves of polymers, where curve 1 is for copolymer III, curve 2 is for copolymer V, curve 3 is for copolymer VI (in air the temperature rise rate is 5 deg/min).

TABLE

Elementary analysis, some physico-chemical properties and yield of copolymers

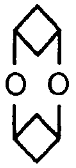
Copolymer No.	*T* reaction °C	Catalyst	sp[a]	*T* soft °C	Å	Elementary composition[b]			Yield %	M 10^3[c]
						C	H	Si		
I	20	H_2PtCl_6	0.04	—	—	$\frac{58.49}{58.87}$	$\frac{4.51}{4.91}$	$\frac{20.88}{21.13}$	80	—
	30	-"-	0.06	—	—				83	—
	40	-"-	0.10	75–85	10.20				84	55
	20	KOH	0.07	74–80	—				91	—
	30	-"-	0.09	—	—				93	—
	40	-"-	0.13	81–87	10.20				94	—
II	40	H_2PtCl_6	0.09	—	—	$\frac{62.60}{62.84}$	$\frac{4.59}{4.73}$	$\frac{18.51}{18.92}$	86	—
	40	KOH	0.12	78–83	10.20				94	61
III	40	H_2PtCl_6	0.07	62–69	—	$\frac{64.99}{65.32}$	$\frac{4.58}{4.81}$	$\frac{17.60}{17.72}$	85	—
	40	KOH	0.10	—	10.57				93	53
IV	40	H_2PtCl_6	0.08	—	—				84	—
	40	KOH	0.10	80–85	10.57	$\frac{61.69}{62.63}$	$\frac{4.73}{4.95}$	$\frac{17.89}{19.23}$	93	—
V	40	H_2PtCl_6	0.06	64–72	10.57	$\frac{64.74}{65.32}$	$\frac{4.65}{4.81}$	$\frac{17.36}{17.72}$	81	—
VI	40	-"-	0.07	65–73	10.57	$\frac{65.01}{65.32}$	$\frac{4.40}{4.81}$	$\frac{17.96}{17.72}$	82	37

[a] In toluene at 25°C.

[b] In denominator there are found values; in numerator there are calculated values.

[c] Molecular masses are found by light diffusion.

It should be noted that in the case of catalytic dehydrocondensation, it is unlikely that the reaction proceed by the mechanism of intramolecular cyclization with formation of the compounds of B structure



(B)*

In the IR spectra of the synthesized compounds one can observe absorption bands characteristic of asymmetric valence oscillations of the linear Su—O—Si bond in the range 1060–1080 cm^{-1}, peculiar to the Si—O—Si bond in the cyclotetra- and hexasiloxane fragments. In the region 1000 and 1435 cm^{-1}, one can observe absorption bands for the Si—Ph bonds. Besides, one can see absorption bands typical for deformation oscillations of the C—H bond in the benzene ring in the range of 700 and 725 cm^{-1}. The absorption bands at 1605–1610 cm^{-1} are

---

*The 1,5-dimethyltetraphenylcyclotetrasiloxane fragment is labeled ◇.

typical for valence oscillations of C=C in the benzene ring, and for Si-Me groups are observed at 1275 cm^{-1}.

The synthesized polymers were analyzed by the X-ray method. As is seen from the diffractograms (Figure 8), in the polymers with cyclotetrasiloxane fragments in the chain one can observe a diffraction maximum d_1 = 10.20 Å typical of the interplane distance between the cyclotetrasiloxane fragments, while for the polymers with cyclohexasiloxane fragments, the value of the interplane distance increases and equals 10.57 Å.

Also, thermogravimetric investigations of copolymers were performed. As is seen from Figure 9, for polymers at 400°C mass losses do not exceed 3–6%; and with temperature rise mass losses regularly increase. The main destruction process proceeds in the range 600–700°C. With an increase in the cycle volume the finite mass losses increases respectively. The copolymers with cyclotetrasiloxane fragments in the chain are characterized by a higher thermal oxidative stability, than those with cyclohexasiloxane fragments, which, in its turn, can be explained by a change in relation of silasesquioxane (T) and siloxane (D) fragments. In the former case T:D = 1:1, while in the latter one T:D = 1:2.

The Table shows the results of elementary analysis, physico-chemical properties and yield of the synthesized copolymers.

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