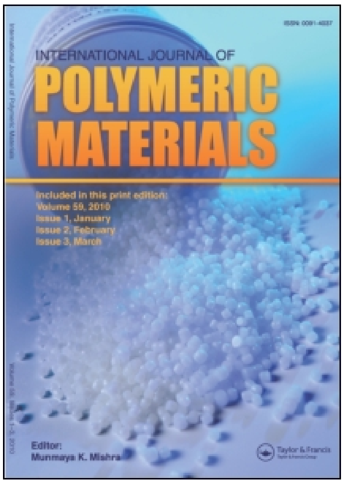

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Lotari M. Khananashvili[a]; Omari V. Mukbaniani[a]; Irma A. Inaridze[a]; Guram V. Porchkhidze[a]; Khatuna E. Koberidze[a]
[a] I. Javakhishvili Tbilisi State University, Tbilisi, Republic of Georgia

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Organosilicon Polycyclic Copolymers of Bead-like Structure

LOTARI M. KHANANASHVILI, OMARI V. MUKBANIANI, IRMA A. INARIDZE, GURAM V. PORCHKHIDZE and KHATUNA E. KOBERIDZE

I. Javakhishvili Tbilisi State University, 3 Chavchavadze Ave., Tbilisi 380028, Republic of Georgia

Catalytic dehydrocondensation of dihydroorganocyclotetra(hexa)siloxanes with dihydroxyorganocyclotetra(hexa)siloxanes in the presence of platinochlorohydric acid on anhydrous powder-like caustic potassium has been studied. High-molecular weight organosilicon polycyclic copolymers with bead-like structure having cyclotetra- and cyclohexasiloxane fragments in the chain and completely insoluble 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 Organosilicon copolymers, polycyclic, thermomechanical characteristics

INTRODUCTION

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

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

Catalytic dehydrocondensation between ≡Si—H containing compounds and hydroxyl containing organic compounds[2,3] proceeds similarly. In these transformations the reaction capacity of the ≡Si—H bond is determined by the nature and amount of the catalyst, the temperature, the concentration of reactants, and the nature of the solvent, etc.[3,4]

During catalytic dehydrocondensation of organohydroxysilanes with organohydroxysilanes catalysts such as colloid nickel, anhydrous zinc chloride, platinochlorohydric acid[5,6] have been used, 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 first time studies[7-9] of the reactions of catalytic dehydrocondensation of hydrid containing organosiloxanes with hydroxy containing organosilanes and siloxanes in the presence of powdered potassium hydroxide as nucleophilic catalyst, showed that under the action of nucleophilic catalysts the competing reaction of dialkylsiloxane elimination does not take place. This has previously been observed,[10,11] and is explained by the high rate of dehydrocondensation. In addition 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 the catalytic dehydrocondensation of linear α, ω-dihydriddiorganosiloxanes with α,ω-dihydroxydiorganosiloxane in the presence of potassium hydroxide, 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 about catalytic dehydrocondensation of hydrid containing organocyclosiloxanes with hydroxyl-containing organocyclosiloxanes. Only the reaction between tetramethylcyclotetrasiloxanes and cis-1,3,5,7-tetrahydroxytetraphenylcyclosiloxanes in the presence of potassium or sodium methylate was studied,[13] and it was established that with an increase in hydrogen conversion the content of insoluble polymer increases.

EXPERIMENTAL PART

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

The purity of the organocyclosiloxanes obtained was verified on a gas-liquid chromatograph "Tsvet-4" or "LMKh-8MD" with SRTP-100 (10%) on NaW chromosorb and He as carrier gas using a 2M column.

Diffractograms were taken on a "DRON-2" instrument. A—Cu were measured without a filter, with angular velocity of the meter $\omega = 2$ deg/min.

The thermomechanical curves were taken on a custom made installation. The test conditions were: $V = 5$ deg/min, $\delta = 0.1$ 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 and weight = 100 mg.

Heterofunctional condensation of methyldichlorosilane with 1,3-dihydroxytetraphenyldisiloxane. To a solution of 11.5 g (0.1 mol) of methyldichlorosilane in 250 ml of anhydrous toluene at room temperature was added 47.4 g (0.7 mol) of 1,3-

dihydroxytetraphenyldisiloxane in 400 ml of anhydrous toluene. The reaction mixture was stirred and heated 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 distillation *in vacuo*, 20 g of I-hydrid-I-methyltriphenylcyclotrisiloxane (I) was isolated having $T_{\text{boil}} = 190–195°\text{C}$, $P = 1 \times 10^{-2}$ 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 $T_{\text{boil}} = 263–267°\text{C}$, $P = 1 \times 10^{-2}$ mmHg, $T_{\text{melt}} = 162–163°\text{C}$ (after recrystallization from hexane), yield: 42%.

The IR bands: 1275 (SiMe); 1435 (SiPh); 1075 (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.

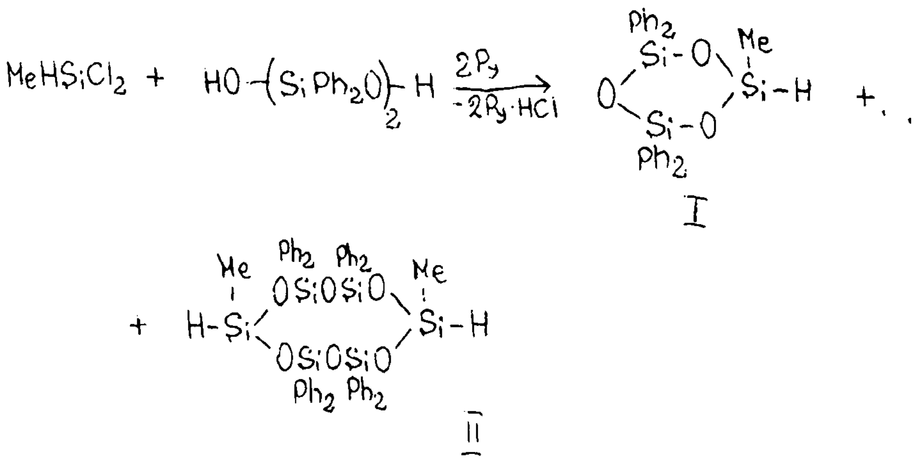
Dehydrocondensation reaction. The catalytic dehydrocondensation reaction was carried out in a two-necked flask equipped with a catalyst inlet tube, and a reflux condensor connected with a gasometer. Between the gasometer and the reflux condensor a cold trap and a wash bottle were installed.

The initial reagents were placed into the flask, dissolved in absolute toluene and thermostatted in an oil bath until a constant temperature was reached. Then the catalyst was introduced. After that hydrogen evolution began. 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 potassium hydroxide was used as a catalyst the reaction products were washed to neutral). The medium was dried over anhydrous Na_2SO_4 and reprecipitated using CH_3OH.

RESULTS AND DISCUSSION

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

1,7-dihydrid-1,7-dimethyloctaphenylcyclohexasiloxane (compound II) was obtained by heterofunctional condensation of methyldichlorosilane with a 1:1 ratio of the initial components in the presence of pyridine 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 a chemical shift in the region of 0.26 and 0.30 ppm, characterizing cis- and trans-isomers. In addition, a singlet 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, 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. In addition, we use a catalytic amount of anhydrous powdered potassium hydroxide as a catalyst.

Preliminary heating of a toluene solution of the initial organocyclosiloxanes (concentration $C = 0.44$ mole/l) over 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 ($\sim 5 \times 10^{-4}$ g per gram of substance) in the temperature range of 40–50°C showed that polymerization and polycondensation of the initial cycles does not take place. Detailed analysis of the reaction solution with gas-liquid chromatography methods has shown the absence of water traces and the presence of hydroorganosiloxanes. In addition, there are no changes in the NMR spectra of organocyclosiloxanes for methyl protons, and in the IR spectra the absorption bands for Si—O—Si bonds (for organocyclosiloxanes) in the range 1070–1080 cm^{-1} are preserved. During the use of 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 of 1–2 min.

Catalytic dehydrocondensation was examined at different temperatures (20, 30 and 40°C) in absolute toluene solution. When the dehydrocondensation reaction in the solution was conducted with anhydrous KOH as a catalyst, the hydrogen conversion increased from 10 to 50%.[6] With a temperature rise during catalytic

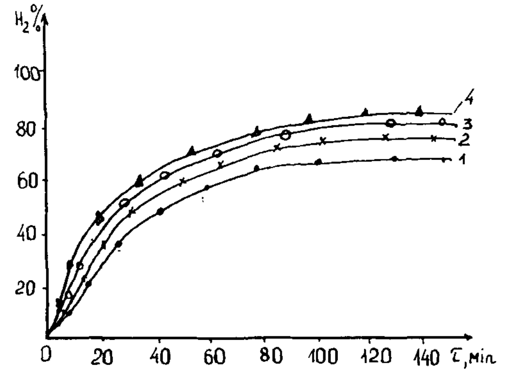
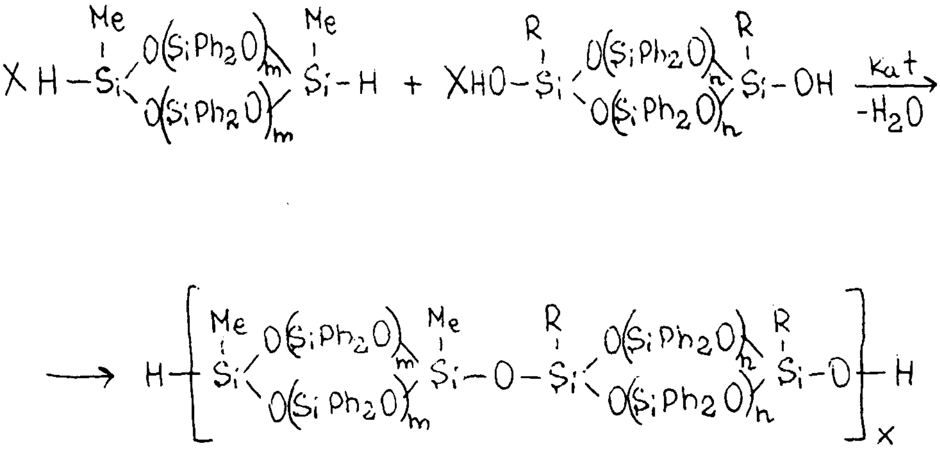


FIGURE 1 Hydrogen release rate in the reaction of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,5-dihydroxy-1,5-dimethyltetraphenylcyclotetrasiloxane, where curve 1 is at 20°C, curve 2 is at 30°C, curve 3 is at 40°C in the case of dehydrocondensation of 1,5-dihydroxy-1,5-dimethyltetraphenylcyclotetrasiloxane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

dehydrocondensation the hydrogen conversion increases from 66% (at 20°C) to 82% (at 40°C) (Figure 1). In order to increase the degree of catalytic dehydrocondensation where platinochlorohydric acid was used as a catalyst, the final stage of the reaction was heated to 70°C for 3–4 h.

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 nature and amount of the catalyst, temperature, the nature of the 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 =Si Me OH (*A*) and =Si Ph 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*′.

$$\sum_{A}^{H(OH)} > \sum_{A'}^{H(OH)}$$

and, consequently, the interaction of the compounds containing fragment *A* with dehydridcyclosiloxanes must be inhibited, but, on the other hand, in fragment *A*′,

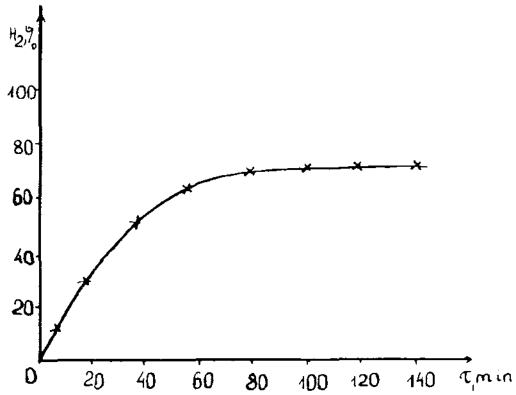


FIGURE 2 Hydrogen release rate during dehydrocondensation of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,7-dihydroxyoctaphenylcyclohexasiloxane at 40°C in the presence of H_2PtCl_6.

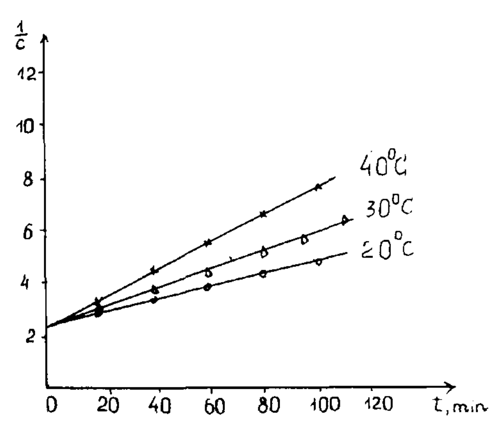


FIGURE 3 Time dependence of the inverse concentration of the reactants (*c* = 0.44 mol/l, catalyst being H_2PtCl_6).

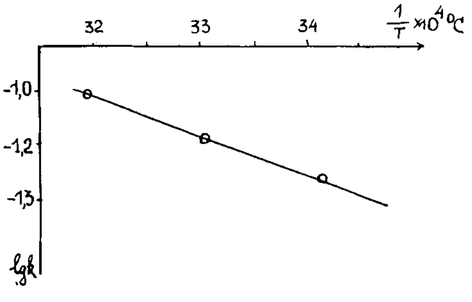


FIGURE 4 Dependence of the reaction rate logarithm on inverse temperature (catalyst being H_2PtCl_6).

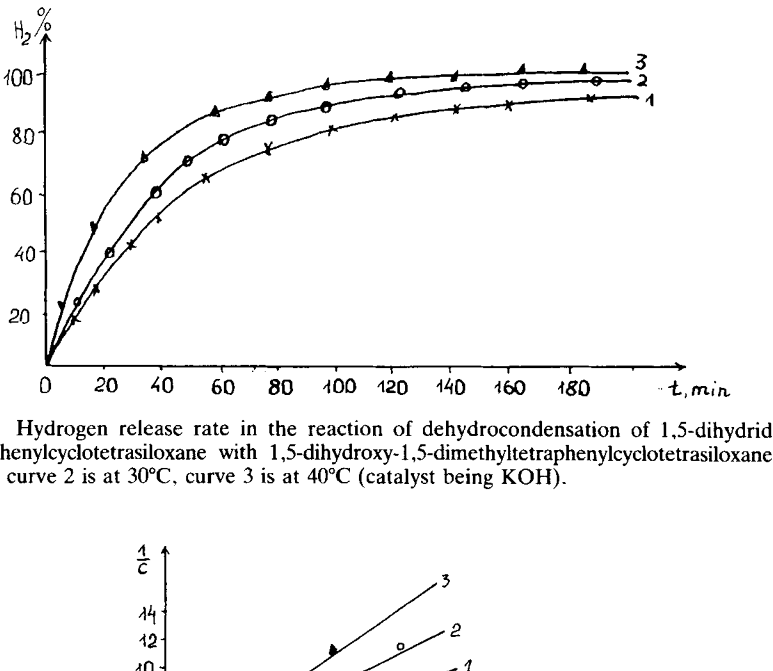


FIGURE 5 Hydrogen release rate in the reaction of dehydrocondensation of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,5-dihydroxy-1,5-dimethyltetraphenylcyclotetrasiloxane; curve 1 is at 20°C, curve 2 is at 30°C, curve 3 is at 40°C (catalyst being KOH).

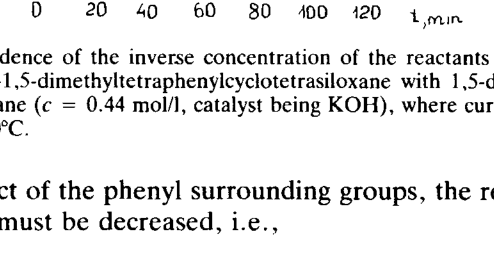


FIGURE 6 Time dependence of the inverse concentration of the reactants upon the dehydrocondensation of 1,5-dihydrid-1,5-dimethyltetraphenylcyclotetrasiloxane with 1,5-dihydroxy-1,5-dimethyltetraphenylcyclotetrasiloxane (c = 0.44 mol/l, catalyst being KOH), where curve 1 is at 20°C, curve 2 is at 30°C,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

due to the steric effect of the phenyl surrounding groups, the reaction capacity of the hydroxyl groups must be decreased, i.e.,

$$S^{\mathrm{H(OH)}} < S^{\mathrm{H(OH)}}$$

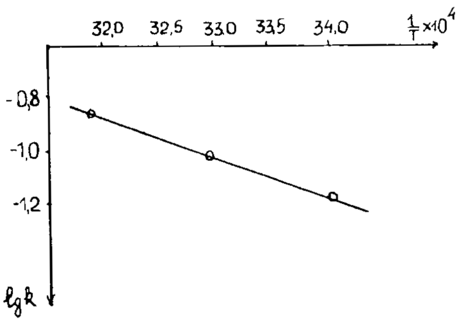


FIGURE 7 Dependence of the reaction rate logarithm on inverse temperature (catalyst being KOH).

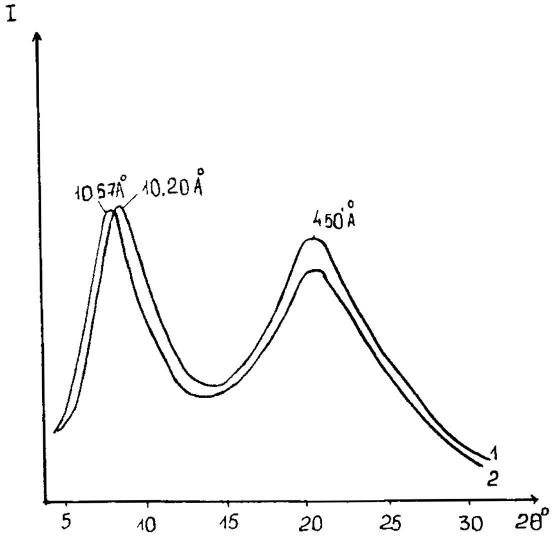


FIGURE 8 Diffractograms of copolymers, where curve 1 is for copolymer III, curve 2 is for copolymer VI.

A *A'*

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

$$\sum_{A}^{\mathrm{H(OH)}} \approx \sum_{A'}^{\mathrm{H(OH)}}$$

It should be noted that in the 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 the rigidity of the polymer chain and enhancement of the steric effect.

The detailed analysis of the reaction products has shown the presence of unreacted organocyclosiloxanes.

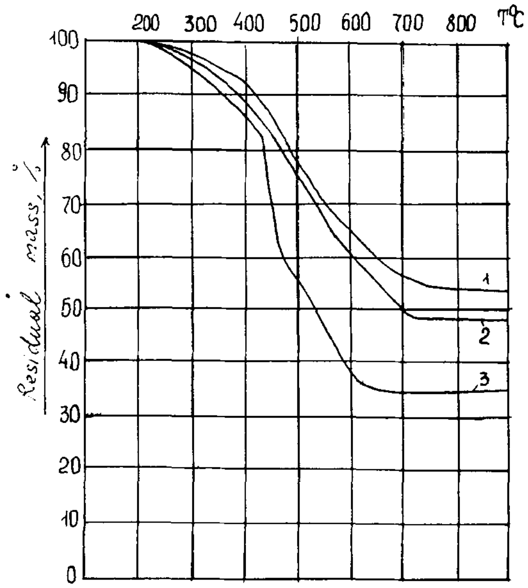


FIGURE 9 The thermogravimetric curves of polymers, where curve 1 is for copolymer III, curve 2 is for copolymer V, curve 3 is for copolymer VI (in air the temperature rise rate is 5 deg/min).

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

Figure 4 shows the dependence of the 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 powdered KOH in absolute toluene. In the course of the reaction the hydrogen conversion was examined over time (Figure 5).

In the case of catalytic dehydrocondensation of 1,5-dihydrid-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: $K_{20^\circ C} = 6.9 \times 10^{-2}$; $K_{30^\circ C} = 9.75 \times 10^{-2}$ and $K_{40^\circ C} = 14 \times 10^{-2}$.

Figure 7 shows the dependence of the reaction rate logarithm on temperature, from which the activation energy was calculated $E_{act} = 28.1$ kJ/mol. Therefore, when both catalysts are used the activation energy is the same.

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 compounds of structure *B*:

(B)

(The 1,5-dimethyltetraphenylcyclotetrasiloxane fragment is labeled ◇.) In the IR spectra of the synthesized compounds one can observe absorption bands characteristic of asymmetric valence oscillations of the linear Si—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. In addition, 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 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 poly-

TABLE I

Elementary analysis, some physical chemical properties and yield of copolymers

Copolymer No.	Temp. of reaction, °C	Catalyst	η_{sp}[a]	T_{soft}, °C	Å	Elementary composition[b] C	H	Si	Yield, %	M 10^{3}[c]
I	20	H_2PtCl_6	0.04	—	—	$\frac{58.49}{58.87}$	$\frac{4.51}{4.91}$	$\frac{20.88}{21.13}$	80	—
	30	H_2PtCl_6	0.06	—	—				83	—
	40	H_2PtCl_6	0.10	75–85	10.20				84	55
	20	KOH	0.07	74–80	—				91	—
	30	KOH	0.09	—	—				93	—
	40	KOH	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	H_2PtCl_6	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 the denominator there are experimental values; in the numerator—calculated values.

[c] Molecular masses are found by light diffusion.

mers 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 300°C, mass losses do not exceed 3–6%; and with increasing temperature mass losses regularly increase. The main destruction process proceeds over the range 400–600°C. With an increase in the cycle volume the finite mass loss increases, respectively. Copolymers with cyclotetrasiloxane fragments in the chain are characterized by a higher thermal oxidative stability, than those with cyclohexasiloxane fragments, which in 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 $T{:}D = 1{:}2$.

Table I shows the results of elementary analysis, physical chemical properties and the yield of the synthesized copolymers.

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