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# Organosilicon Copolymers with Carbotricyclodecasiloxane Fragments in the Dimethylsiloxane Chain

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The reaction of stage heterofunctional condensation of *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclo-tetrasiloxane (tetrol) with 1,3-dichlorotetramethyldisiloxane and 1,3-dichlor-1,3-dimethyl-1,3-divinyldisiloxane by the ratio of initial products of 1:1:1 has been studied in the presence of pyridin and 1,3-divinyl-1,3,9,9,11,11-hexamethyl-5,7,13,15-tetraphenyltricyclodecasiloxane has been obtained. The reaction of hydrid polyaddition of  $\alpha,\omega$ -dihydriddimethylsiloxanes to 1,3-divinyl-1,3,9,9,11,11-hexamethyl-5,7,13,15-tetraphenyltricyclodecasiloxanes in the presence of platinochlorohydric acid and acetylacetonat-dicarbonyl rodium catalyst has been studied. The reaction order, activation energies and hydrid polyaddition rate constants have been found. It has been established that with an increase of the length ( $n$ ) of the  $\alpha,\omega$ -dihydriddimethylsiloxanes the degree of hydrid polyaddition is reduced. It was shown that in the case of acetylacetonatdicarbonyl rodium the obtained copolymers are structured. Thermogravimetric, thermomechanical and X-ray studies of the synthesized copolymers have been carried out.

**KEY WORDS** Organosilicon copolymers, carbotricyclodecasiloxane, dimethylsiloxane.

## INTRODUCTION

It is known, that the synthesis of carboorganosiloxane oligomers and polymers is based on the reaction of hydrid polyaddition of organohydriddisiloxanes to organo-alkenylsiloxanes.<sup>1</sup> It is possible, employing this reaction to obtain the oligomers and polymers of linear structure,<sup>2–4</sup> as well as the polymers of cycloliner structure with eight membered fragments in the chain.<sup>5,6</sup>

It was shown, that by the introduction of cyclocarbosiloxane fragments into dimethylsiloxane chain the thermal-oxydative stability of cycloliner copolymers increases.

Polycarbosiloxanes with methylcyclotetrasiloxane ethylen-bridged links have been obtained by the reaction of self-polyaddition of 1-hydrid-3-vinylhexamethylcyclotetrasiloxane.<sup>7</sup>

The carbosiloxane copolymers comprising in the chain organocyclotetra(penta, hexa)siloxane fragments have been synthesized by the reaction of hydrid poly-

addition of dihydroorganocyclotetra(penta,hexa)siloxanes to divinylorganocyclotetra(penta,hexa)siloxanes.<sup>8,9</sup> It was established, that the thermal stability of the copolymers declines with an increase of the volume of the cyclosiloxane ring.

Compared to polyorganosiloxane analogs, the polymers with disilylethylenic groups have lower thermal-oxidative stability, but higher thermal stability in absence of oxygen.<sup>8,10</sup>

## EXPERIMENTAL PART

The purity of all the initial organochlorosilanes and siloxanes have been controlled by their boiling temperatures, chlor ions content and refraction indexes.

The organic solvents were cleaned by drying and distillation.

The initial  $\alpha,\omega$ -dihydriddimethylsiloxanes have been synthesized by well-known methods.<sup>11</sup>

IR spectra of all the samples have been taken on an UR-20 instrument, while the NMR spectra-on a "Perkin Elmer" R-32 at operating frequency of 90 MHz in the solutions of  $\text{CCl}_4$  and dioxane HMDS or TMS as internal standard.

The purity of obtained divinyl containing organocyclosiloxane was verified on a gas-liquid chromatograph "λXM-8MΔ" phase SKTF-100 (10%), the NAW chromosorb, carrier gas—He, the 2M column.

Diffractionograms were taken on a "ΔPOH-2" instrument,  $A\text{-Cu}_\alpha$  values 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 was carried out as follows:  $V = 5$  deg/min,  $\delta = 0.1$  kg/sm<sup>2</sup>.

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

### Heterofunctional Condensation of cis 1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane (Tetrol) with 1,3-dichlortetramethyldisiloxane and 1,3-dichlor-1,3-divinyl-1,4-dimethyldisiloxane

To a solution of 27.6 g (0.05 mole) of tetrol in 500 ml of anhydrous ether at room temperature a solution of 10.1 g (0.05 mole) of the 1,3-dichlortetramethyldisiloxane in 25 ml anhydrous ether and a solution of 7.9 g (0.1 mole) of anhydrous pyridin in 25 ml of anhydrous ether were added.

The reaction mixture was stirred and heated at reflux for 3–4 h. The residue was filtered off, the solvent was evaporated and 36.5 g of a viscous residue was obtained. After distillation of 29.0 g of product in vacuo, 15.7 g (54%) of pure product was isolated,  $T_{\text{boil}} = 245\text{--}250^\circ\text{C}$ ,  $P = 2\text{--}3 \times 10^{-3}$  mmHg. 14.4 g (92%) 1,3-divinyl-1,3,9,9,11,11-hexamethyl-5,7,13,15-tetraphenyltricyclodecasiloxane was obtained after recrystallization from the mixture toluene-heptane (30:70). IR bands: 1275 (SiMe); 1000, 1435 (SiPh); 1080 (SiOSi); 2900–3000 (C—H).

Calculated for  $\text{C}_{34}\text{H}_{44}\text{Si}_8\text{O}_{10}$ , %: C 44.76; H 5.29; Si 26.83;  $M = 837$ .

Found: C 48.62; H 5.10; Si 27.07;  $M = 800$ .

### Hydrid Polyaddition

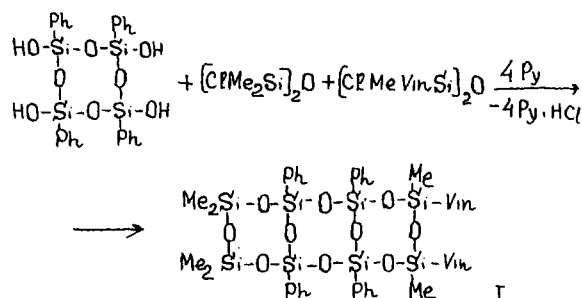
The hydrid polyaddition reaction was carried out in three-necked flask equipped with stirrer and reflux condenser with a chlorcalcium tube. The initial reagents were placed into the flask and thermostated in an oil bath until constant temperature was achieved. For the polymer synthesis, 0.01 M solution of platinochlorohydric acid or 0.1 N solution of acetylacetonatdicarbonyl rodium in tetrahydrofuran ( $5-10 \times 10^5$  g per Ig of the starting substance) was used as a catalyst. The reaction was performed in the argon atmosphere at a 1:1 mole ratio of the starting substances without solvent at temperatures of 70, 80 and 90°C.

The reaction proceeded in dry argon ambient 7–8 h. Then the reaction mixture was diluted in toluene, filtered off and precipitated by addition of methyl alcohol.

### RESULTS AND DISCUSSION

The present paper deals with synthesis and studies of the properties of carbosiloxane copolymers contained in the chain along with dimethylsiloxane fragments tricycloorganodecasiloxane fragments. There are no data in the literature on the carbosiloxane copolymers of the above mentioned structure.

For the purpose of synthesis of 1,3-divinyl-1,3,9,9,11,11-hexamethyl-5,7,13,15-tetraphenyltricyclodecasiloxane (I) the reaction of heterofunctional condensation of cis-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane with 1,3-dichlorotetramethylsiloxane and 1,3-dichlor-1,3-divinyl-1,3-dimethylsiloxane was carried out in the presence of pyridin with 1:1:1 ratio of the initial components in the diluent solution of the anhydrous ether. After distillation and recrystallization of the obtained product 1,3-divinyl-1,3,9,9,11,11-hexamethyl-5,7,13,15-tetraphenyltricyclodecasiloxane (I) was obtained according to the following scheme:



The composition and structure of synthesized compound I were determined by means of functional and elementary analysis, by finding of molecular mass, by IR and NMR spectra data.

In the  $^1\text{H}$  NMR spectra of compound I one can observe two signals with chemical shifts of  $\delta = 0.55$  and  $\delta = 0.75$  ppm, for Si—Me protons, multiplet in the region 7.5–8.2 ppm for phenyl protons and multiplet for vinyl protons with center of the signal at 6.2 ppm.

In the IR spectra of compound I one can observe absorption bands characteristic

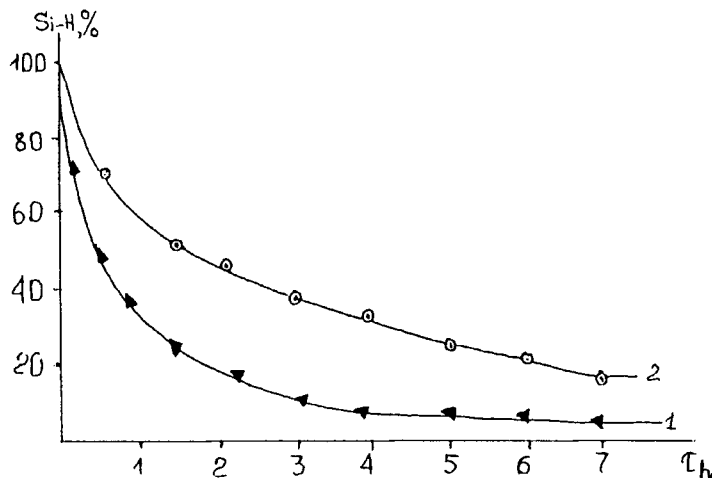


FIGURE 1 Change in Si—H(%) with time upon polyaddition of  $\alpha,\omega$ -dihydriddimethylsiloxane to divinylorganotricyclodecasiloxane at 90°C, where curve 1 is for  $n = 4$ , curve 2 is for  $n = 12$ .

of asymmetric stretching vibrations of the Si—O—Si bands in the region of 1050 and 1080  $\text{cm}^{-1}$ . One can also observe absorption bands for Si—Me, Si—Ph and Si—Vin bonds in the region of 1275, 1435 and 2900–3000  $\text{cm}^{-1}$  respectively.

The polymer synthesis was carried out at temperatures not exceeding 90°C, so that cyclosiloxane ring opening would not take place in the conditions of hydrid polyadditions.

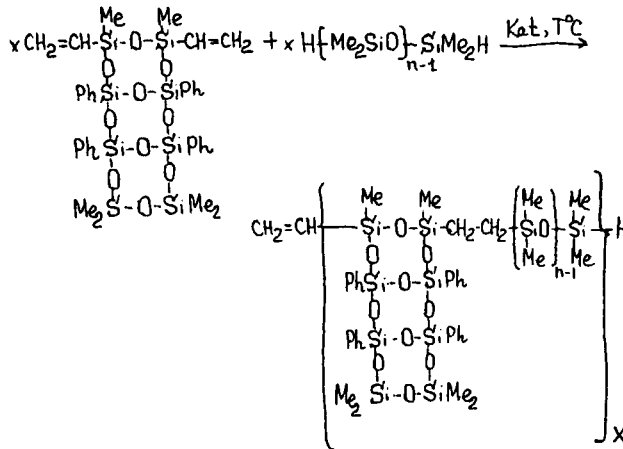
Preliminary heating of divinylorganotricyclodecasiloxane (I) within the temperature range of 70–90°C for 10 h in the presence of acetylacetonatdicarbonyl rodium or platinochlorhydric acid as a catalyst showed, that in this condition polymerization of the starting divinyltricyclodecasiloxane did not occur. The detailed analysis of the reaction mixture by gas-liquid chromatography method has been shown the presence of initial organosiloxanes. Besides, there are no changes in the NMR and IR spectras of compound I and dihydriddimethylsiloxanes.

The hydrid polyaddition reaction of compound I was carried out employing various lengths of  $\alpha,\omega$ -dithdriddimethylsiloxanes. The course of the reaction was watched by decrease of amount of active Si—H groups. It was established, that in the case of using of rodium acetylacetonatdicarbonyl as a catalyst obtained in organic solvents soluble copolymers, which during a time structured. This may be explained that in spite of the polymers reprecipitated from toluene solution by methyl alcohol, catalyst of rodium remained in polymeric systems, which decompose and evoke a decomposition of copolymers.

Therefore for receipt of copolymers we used as a catalyst platinochlorohydric acid.

It was observed, that with the increase of length of  $\alpha,\omega$ -dihydriddimethylsiloxane chain the rate and depth of the polyaddition reaction decreases. As it is shown in Figure 1 the conversion of Si—H bond is not completely and decreases from 95% ( $n = 4$ ) to 83% ( $n = 12$ ).

The reaction of hydrid polyaddition proceeds according to the general scheme:



where  $n = 2(\text{II}), 4(\text{III}), 6(\text{IV}), 12(\text{V}), 21(\text{VI})$ . Catalyst— $\text{H}_2\text{PtCl}_6$ .

As a result of the reaction, copolymers are obtained with  $\eta_{\text{spec}} = 0.08-0.26$ , that are liquid or vitreous light yellow transparent products soluble in usual organic solvent. Some physico-chemical properties, elementary composition, molecular weight and yields of synthesized copolymers are presented in the Table I.

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

Copolymer	T react °C	η spec	T vitr. °C	d <sub>1</sub> , g	Elementary composition <sup>†</sup>			Yield, %	M <sup>†</sup> × 10 <sup>3</sup>
					C	H	Si		
II	90	0,08	-12	10,20	<u>47,31</u>	<u>5,99</u>	<u>29,01</u>	80	72
					47,01	5,92	28,86		
III	70	0,09	-	-	<u>45,21</u>	<u>6,21</u>	<u>29,86</u>	83	-
					45,08	6,06	30,05		
III	80	0,10	-	-	<u>44,96</u>	<u>6,11</u>	<u>30,26</u>	88	-
					45,08	6,26	30,05		
III <sup>3</sup>	90	0,11	-50	-	<u>45,31</u>	<u>6,19</u>	<u>30,35</u>	91	85
					45,08	6,26	30,05		
IV	90	0,14	-96	8,68	<u>43,67</u>	<u>6,06</u>	<u>31,10</u>	92	-
					43,60	6,47	30,96		
V	90	0,20	-123	-	<u>41,43</u>	<u>6,86</u>	<u>32,70</u>	93	-
					41,10	6,73	42,51		
VI	90	0,26	-123	7,54	<u>56,61</u>	<u>4,89</u>	<u>23,73</u>	94	110
					56,74	5,08	23,99		

<sup>†</sup>In toluene at 25°C; †In denominator found values; in numerator calculated values. †Molecular masses are found gel chromatographic method.

The course of the reaction was controlled also, by an increase in viscosity of obtained copolymers. It was established that with increase of temperature to 70–90°C the viscosity of copolymers rises.

It was observed, that with temperature rise in the reaction of hydrid polyaddition of compound I with  $\alpha,\omega$ -dihydriddimethylsiloxane the conversion of Si—H bond increases from 85% (70°C) to 95% (90°C).

Figure 2 shows dependence of the Si—H% concentration decrease on the time. Figure 3 shows the direct dependence of reverse concentration of the reactant on the time. One can see, that the hydrid polyaddition is the reaction of second order. Proceeding from the data of Figure 3 the reaction rate constants at various temperatures were calculated:  $k_{70^\circ\text{C}} = 1.1086 \times 10^{-2}$ ,  $k_{80^\circ\text{C}} = 1.6196 \times 10^{-2}$ ,  $k_{90^\circ\text{C}} = 2.3834 \times 10^{-2}$ . It was found that each time with an increase of the reaction temperature by 10°C the reaction rate constants increases approximately 1.5 times.

Figure 4 shows the dependence of the reaction rate constants logarithm on reverse temperature, from which data the activation energy of the hydrid polyaddition reaction has been calculated to be equal to 64.4 KJ/mole.

The analysis of the IR spectra of the obtained copolymers revealed, that the absorption bands characteristic for Si—H bonds in the range of 2160–2170  $\text{cm}^{-1}$  do not vanish completely. The new absorption bands appear in the spectra at 1150  $\text{cm}^{-1}$ , typical for *g* fan shaped oscillations of the  $\text{CH}_2$  groups, as well as absorption bands in the range of 2900–3000  $\text{cm}^{-1}$ , typical for valence oscillations of the CH bonds in the  $\text{CH}_2$  groups of the ethylenic bridges.

By  $^1\text{H}$  NMR spectra for copolymer II it has been established, that catalytic hydrid polyaddition proceeds mainly by the Farmer rule with formation of dimethylenic bridges. In NMR spectrum one can observe a signal for grouping  $-\text{CH}_2-\text{CH}_2-$  with the chemical shift of  $\delta = 0.32$  ppm. One can observe also a double signal with chemical shift center at  $\delta = 1.12$  ppm, which can be assigned to methyl proton in the grouping  $=\text{CH}-\text{CH}_3$ , whose amount is about 5–6%. Integral relations of methyl and phenyl protons correspond to the formula of the copolymer II.

Thermomechanical studies of the obtained copolymers have been carried out and it was established, that vitrification temperature of copolymers decreases with an increase of the value  $n$  of the linear dimethylsiloxane chain (Figure 5). Beginning from value of  $n = 11$  the influence of carbocyclodecasiloxane fragments in copolymers does no more effect on dimethylsiloxane chain and the vitrification temperature for copolymer V remains of  $-123^\circ\text{C}$ .

The increase of the dimethylsiloxane chain length ( $n = 21$ ) does not lead to the formation two-phase system as it was shown early by us,<sup>12</sup> in cycloliner copolymers containing rigid tricyclodecaphenyldecasiloxane and flexible dimethylsiloxane links.

Comparative estimation of vitrification temperature of carbocyclodecasiloxane fragments containing copolymers with tricyclodecasiloxane containing copolymers,<sup>12</sup> shows, that they are characterized by lower values of vitrification temperature, which may be explained by additional presence of flexible  $-\text{CH}_2-\text{CH}_2-$  groups in copolymers.

The thermogravimetric investigation of copolymers has been carried out. These investigations have shown (Figure 6), that in case of low values of dimethylsiloxane chain  $n$ , the copolymers are characterized with higher thermooxidative stability. With an increase of the length of dimethylsiloxane chain the thermooxidative stability of

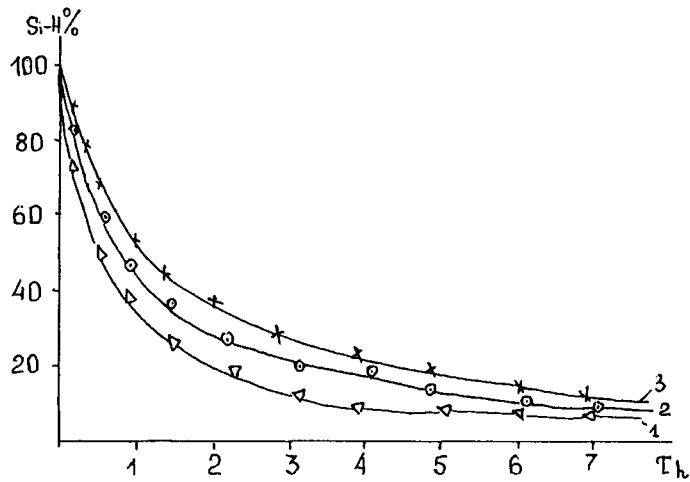


FIGURE 2 Change in Si—H(%) with time upon polyaddition of  $\alpha,\omega$ -dihydriddimethylsiloxane ( $n = 4$ ) to divinylorganotricyclodecasiloxane, where curve 1 is for temperature 90°C, curve 2 is for 80°C, curve 3 is for 70°C.

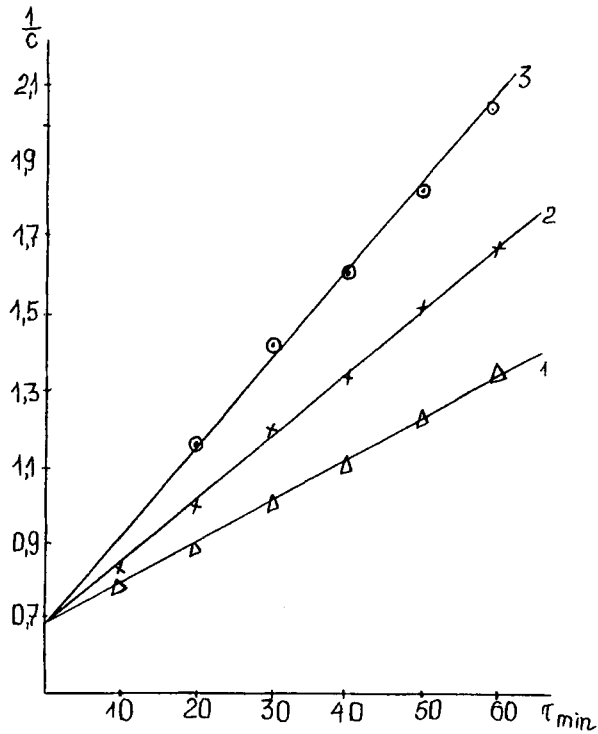


FIGURE 3 Dependence of reverse concentration in time. Curve 1 is for 70°C, curve 2 is for 80°C, curve 3 is for 90°C.



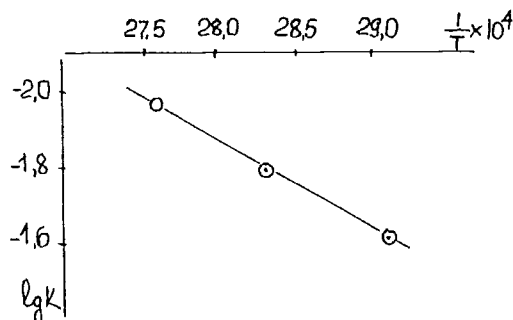


FIGURE 4 Dependence of reverse temperature on the logarithm of the rate constant of the polyaddition reaction.

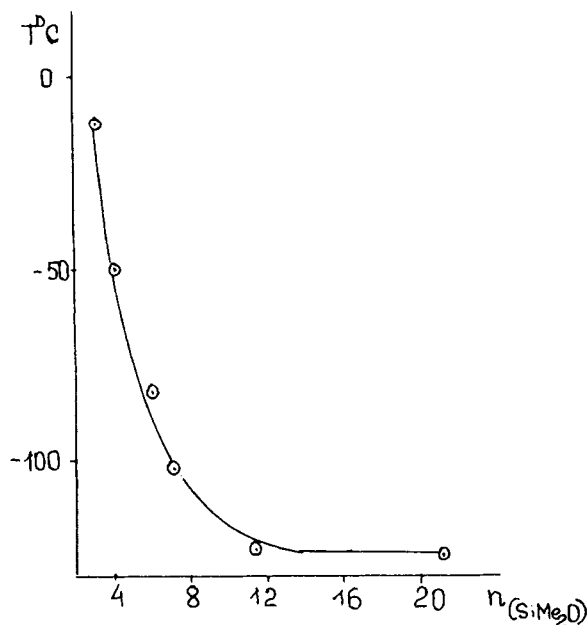


FIGURE 5 Dependence of vitrification temperature of cycloliner copolymers on the length  $n$  of the linear polydimethylsiloxane.

copolymers decreases. With their thermooxidative stability carbocyclodecasiloxane containing copolymers cede to its siloxane analogies.<sup>12</sup> For polymer mass losses in temperature interval 300–350°C do not exceed 3–7% and the main distribution process proceeds in the range 400–650°C. Above 650°C the curves of mass losses do not change (Figure 6).

By the introduction of carbocyclodecasiloxane fragments in dimethylsiloxane chain the main destruction process proceeds approximately at 80–100°C higher temperature than the main destruction of unblocked polydimethylsiloxane.

The synthesized copolymers were analyzed by the roentgenographic method. As can be seen from the amorphous polymer diffractograms (Figure 7) in the case of a

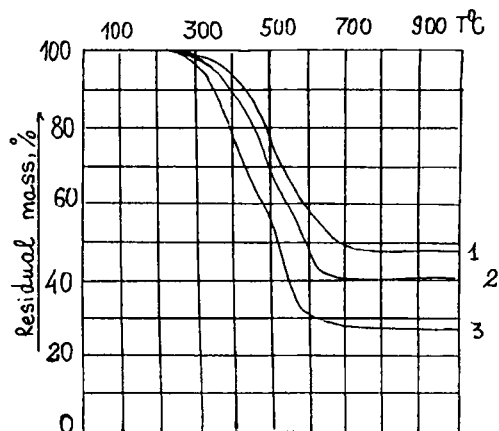


FIGURE 6 Thermogravimetric curves of cyclolinar carbosiloxane copolymers, where curve 1 is for copolymer II, curve 2 is for copolymer IV, curve 3 is for copolymer VI (in air, the rate of temperature increase is 5 deg/min).

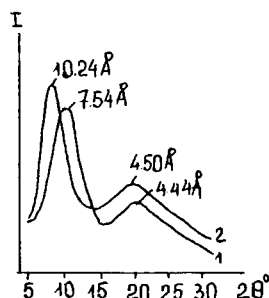


FIGURE 7 Diffractograms of copolymers, where curve 1 is for copolymer VI, curve 2 is for copolymer II.

small values  $n$  the interchain distance reached its maximum value  $d_i = 10.24 \text{ \AA}$ , with an increase of a length dimethylsiloxane chain  $n = 21$ , interchain distance decreases and for copolymer VI  $d_i = 7.54 \text{ \AA}$ . So in copolymer VI does not occur formation two-phase systems, as it was observed in copolymers with decaphenyl-tricyclodecasiloxane fragments in dimethylsiloxane chain, may be explained in our case by combination of the rigid carbocyclosiloxane and flexible dimethylsiloxane fragments therefore the copolymers are a single-phase systems.

So, by means of the reaction of hydrid polyaddition we have synthesized and studied, for the first time, the properties of carbosiloxane cyclolinar copolymers, containing reactionable tricyclodecasiloxane fragments with regular arrangement in the chain. Such copolymers may be structured without giving of gaseous products.

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