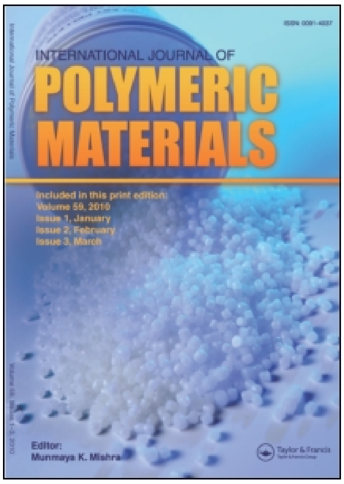

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Carbosiloxane Cyclolinear Copolymers with 1, 7-Arrangement of Organocyclohexasiloxane Fragments in the Main Dimethylsiloxane Chain

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By means of a reaction of heterofunctional condensation we obtained 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane. The reaction of hydrid polyaddition of α,ω-dihydriddimethylsiloxanes to 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane in the presence of platinium chlorhydric acid as a catalyst has been studied. The reaction order, activation energies and hydrid polyaddition rate constants have been found. Thermogravimetric, thermomechanical and X-ray analysis of synthesized carbosiloxane copolymers have been carried out.

Keywords: Carbosiloxane copolymers; hydrid polyaddition; organocyclohexasiloxane; thermal-oxidative stability

INTRODUCTION

Carbosiloxane oligomers and copolymers can be obtained by hydrid polyaddition reactions of dihydridorganosiloxanes to divinylorganosiloxanes [1]. Employing this reaction it is possible to obtain the

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*Corresponding author.

oligomers and copolymers of linear structure [2, 3], as well as the copolymers of cyclolinear structure of macromolecules [4]. Cyclolinear polyorganosiloxanes containing organocyclotetrasiloxane fragments in the chain were synthesized by reaction of hydrid polyaddition of α, ω-dihydriddimethylsiloxanes to 1,3-divinylhexamethylcyclotetrasiloxane and 1,5-divinylhexamethylcyclotetrasiloxane [5]. Copolymers with 1,5-arrangement of the organocyclotetrasiloxane fragments in the chain were synthesized by reaction of hydrid polyaddition of 1,5-dihydridorganocyclotetrasiloxanes to 1,5-divinylorganocyclotetrasiloxanes [5]. Carbosioxane copolymers with ethylene bridges between the cyclic fragment with 1,3-arrangement of cyclotetrasiloxane fragments were synthesized by hydrid polyaddition of 1,3-dihydridorganocyclotetrasiloxanes to 1,3-divinylorganocyclotetrasiloxanes in the presence of platinium chlorhydric acid as a catalyst [6]. It was shown that the polyaddition reaction proceeds with formation of a β-adduct. The reactivity of the active (vinyl, hydrid) groups in cyclotetrasiloxanes in reaction of hydrid polyaddition depends on their position in the cycle. Polymers with higher molecular masses are formed by interaction of cycles with 1,5-position of functional groups. Carbosiloxane copolymers with 1,3-arrangement of hexamethylcyclotetrasiloxane fragments were synthesized by reaction of self addition of 1-hydrid-3-vinylhexamethylcyclotetrasiloxane in the presence of the Spyer catalyst [4]. Carbosiloxane copolymers with ethylenebridges between the cyclic fragments were synthesized by hydrid polyaddition of dihydridorganocyclotera(penta, hexa)siloxanes to divinylorganocyclopenta(hexa)siloxanes. It was shown that with an increase in cycle volume the rate of hydrid polyaddition reaction decreases [7].

Organocyclocarbosiloxane copolymers with tricyclodecasiloxane fragments in dimethylsiloxane chain were obtained by hydrid polyaddition of α,ω-dihydriddimethylsiloxanes to 1,3-divinyl-1,3,9,9,11,11-hexamethyl-5,7,13,15-tetraphenyltricyclodecasiloxane in the presence of platinium chlorhydric acid and acetylacetonatdicarbonyl rodium. It was shown that in the case of rodium catalyst the obtainc copolymers are structured [8].

EXPERIMENTAL PART

The starting materials for the synthesis of carbosiloxane copolymers with cyclohexasiloxane fragments in the chain were 1,7-dichloro-1,7-

divinyl-1,7-dimethyltetraphenyltetrasiloxane and 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane, obtained by well-known methods [9, 10].

The organic solvents were purified by drying and distillation. The purity of the starting compounds was controlled by gas-liquid chromatography "ΛXM-8 MΔ", phase SKTF-100 (10%), the NAW chromosorb, carrier gas-He, the 2 M column.

IR spectra of all samples have been taken on an UR-20 instrument, while the ^{1}H NMR spectra on a "Perkin-Elmer" *R*-32 at operating frequency of 90 MHz in the solutions of CCl_4 and dioxane HMDS or TMS as internal standard.

Diffractograms were taken on a "ΔPOH-2" instrument, $A - Cu_a$ values were measured without a filter, the angular velocity of the motor $w = 2$ deg/min.

The thermomechanical investigations were carried out 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" derivaograph model MOM-102. The test conditions were: temperature rise rate $V = 5$ deg/min weight $m = 100$ mg.

Heterofunctional Condensation of 1,7-Dichlor-1,7-Divinyl-1,7-Dimethyltetra-Phenyltetrasiloxane with 1,3-Dihydroxytetraphenyldisiloxane

To the solution of 46,7 g (0,075 mole) of 1,7-dichlor-1,7-divinyl-1,7-dimethyltetraphenyltetrasiloxane in 900 ml anhydrous toluene at 0–5°C temperature, the solution of 31,0 g (0,075 mole) of 1,3-dihydroxytetraphenyldisiloxane in 100 ml anhydrous toluene and the solution of 11,9 g (0,15 mole) pyridin in 30 ml anhydrous toluene were added. The reaction mixture was stirrered and heated at reflux for 3–4 h. The residue was filtered off, the solvent was evaporated and 68 g of a viscous product was obtained. After distillation of 68 g product in vacuo 45 g (66%) a semi cristalline product I was isolated with $T_{boil} = 300-305°C$, $P = 2-3 \times 10^{-2}$ mmHg. After recrystallization from toluene-heptane solution 42 g (62%) of crystalline product were obtained with $T_{melt} = 62-65°C$ and IR bands 1275 (SiMe), 1000, 1445 (SiPh), 1020, 1075 (SiOSi), 2900–3000 (CH).

Calculated for $C_{54}H_{52}Si_6O_6$,%: C 67, 17; H 5, 43; Si 17, 46; $M=965$. Found %: C 66, 95; H 5, 31; Si 17, 23; $M=929$.

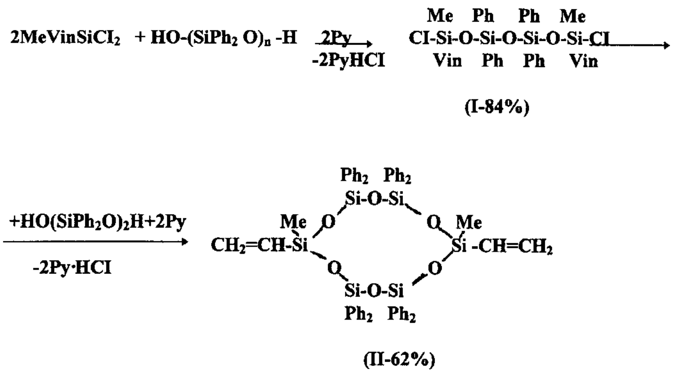
Hydrid Polyaddition

The hydrid polyaddition reaction was carried out in the tree-necked flask equipped with stirrer and reflux condenser, with calcium chloride tube. The initial reagents were placed into the flask and thermostated in an oil bath until constant temperature was achieved. For the polymer syntheses 0,01 M solution of platiniumchlorhydric acid in tetrahydrofurane $(5-10\times10^{-5}$ g per 1 g of the starting substance) was used as a catalyst. The reaction was performed in the argon atmosphere at 1:1 ratio of the starting substances in the presence of toluene, at temperatures 80, 85 and 90°C. Then the reaction mixture was diluted in toluene, filtered off and reprecipitated by addition of methanol.

RESULTS AND DISCUSSION

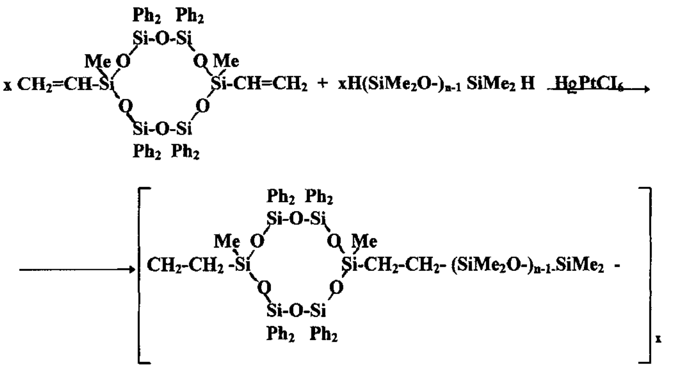
In literature there is no information about cyclolinear carbosiloxane copolymers with 1,7-dimethyloctaphenylcyclohexane fragments in the main dimethylsiloxane chain. The initial compound 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane early was obtained by us, by heterofunctional condensation (HFC) of methylvinyldichlorsilane with 1,3-dihydroxytetraphenyldisiloxane with the ratio 1:1 of initial components in the presence of pyridin [11]. The HFC was carried out in one stage and the yeild of 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane was about 23%. For the purpose of synthesis of 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane with higher yeild, the synthesis was carried out in a two stage reaction, according to the following scheme:

The composition and the structure of compound II was determined by means of elementary analysis, by finding the molecular mass, by IR and ^{1}H NMR spectra, which are in agreement with literature data [11]. The synthesized compound II contains isomeric cis- and transforms in the ratio 52, 5:47, 5.



SCHEME I

The hydrid polyaddition of α,ω-dihydriddimethylsiloxanes to 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane in presence of platinum chlorohydric acid was carried out below 100°C. Preliminary heating of 1,7-divinylcyclohexasiloxane II within the temperature range of 80–95°C in the presence of catalyst, showed that at this conditions polymerization of organocyclohexasiloxane does not take place. Besides, there are no changes in the NMR and IR spectra of compound II and α,ω-dihydriddimethylsiloxanes. The reaction of hydrid polyaddition of compound II with α,ω-dihydriddimethylsiloxanes proceeds according to the following scheme:



SCHEME II

where: $n = 2$ (III), 4 (IV), 6 (V), 12 (VI), 23 (VII).

Since the initial compound II contained a mixture of a cis-and trans-isomers, and in the formation of macromolecular chain both isomers take place, the synthesized copolymer has an atactic structure. From literature it is known [11], that the copolymers which contain only cis- or trans - structures, are characterized by the same thermomechanical properties and thermal-oxidative stability. Therefore, in synthesized atactic copolymers, cis - and trans - structure of cyclic fragments does not influence the physico-chemical properties of copolymers.

The reaction of hydrid polyaddition was carried out at the various temperatures; 80, 85 and 90°C. The course of the reaction was observed by decrease of the amount of active Si—H groups. As it is shown in Figure 1, with the rise of temperature the rate of hydrid polyaddition increases (at one and the same values of dimethylsiloxane links *n*), but in another side with an increase of the length of dimethylsiloxane links (*n*) at the same values of temperature, the rate of hydrid polyaddition decreases. Form the Figures 1 and 2 we see that the conversion of active Si-H groups is not complete and decreases

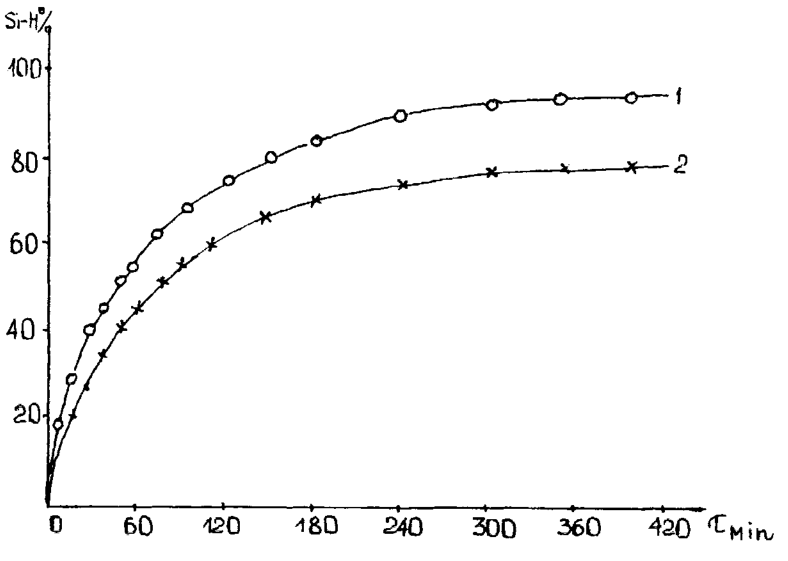


FIGURE 1 Dependence of changes of active Si—H% groups on the time upon polyaddition of α,ω-dihydriddimethylsiloxanes to 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane at 90°C, where curve 1 is for $n = 6$, curve 2 is for $n = 23$.

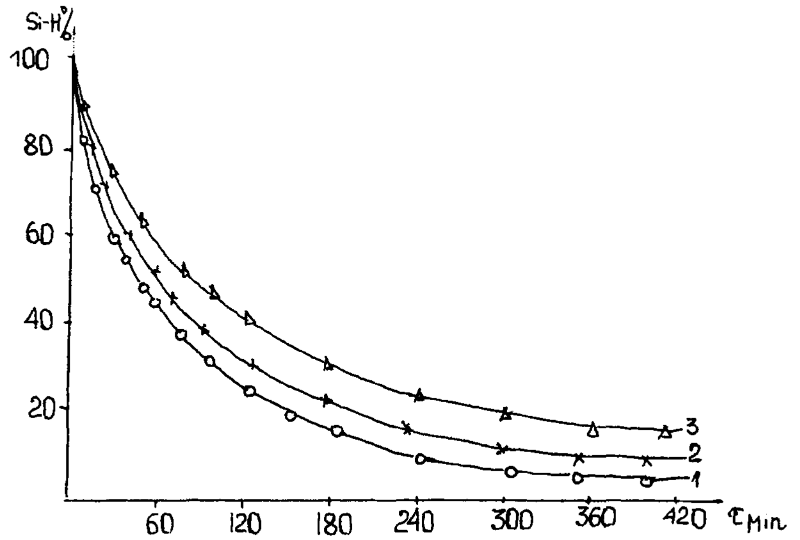


FIGURE 2 Dependence of changes of active Si—H% groups on time upon polyaddition of α,ω-dihydriddimethylsiloxane ($n=6$) 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane, where curve 1 is at 90°C, curve 2 is at 85°C and curve 3 is at 80°C.

from 94% ($n=6$) to 82% ($n=23$). The synthesized copolymers are liquid or vitreous light yellow transparent products soluble in ordinary organic solvents with $\eta_{spec}=0{,}10\div 0{,}29$. Some physico-chemical properties, elementary composition, molecular weight and yields of synthesized copolymers are presented in Table I.

As it is shown in Table I at a small values of the length of dimethylsiloxane links ($n \leq 4$) the yields of copolymers after

TABLE I Some physical-chemical properties and yields of carbosiloxane copolymers

copolymer N	*yield %*	*react temp. °C*	*spec.*	*d_I, Å*	*5% mass losses*	*Resid. mass*	*T_{vitr} °C*	*$M\times 10^3$*
III	74	90	0,10	9,31	280	25	5	174
IV	80	90	0,12	–	–	–	−10	–
V′	95	90	0,18	8,81	280	22	−40	194
V″	94	85	0,17	–	–	–	–	–
V‴	94	80	0,17	–	–	–	–	–
VI	96	90	0,23	8,40	–	–	−68	–
VII	95	90	0,29	7,24	260	18	−123	231

In toluene at 25°C.

reprecipitation from toluene solution by methanole are lower, which may be explained by intramolecular cyclization, where the part of cis structure of starting 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane promotes the formation of bicyclic structures, while the trans structure is responsible for formation of polymeric products. After reprecipitation of copolymer III from toluene solution by methanol, from mother solution we obtained semicrystalline product with molecular weight of ~ 1250. This molecular mass corresponds to the product which may be obtained by intramolecular cyclization, during hydrid polyaddition of 1,3-dihydridtetramethyldisiloxane to *cis*-1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane, which is in agreement with literature data [12].

The IR spectra of copolymers revealed that the absorption bands characteristic for Si—H bounds in the range 2160–2170 cm^{-1} do not vanish completely. One can also observe the absorption bands at 1075 and 1020 cm^{-1}, characteristic for assymetric valence thylsiloxane, The new absorbtion bands appears in the spectra at 1150 cm^{-1}, typical for fan-shaped oscilations of CH_2 groups, as well as absorption bands in the range 2900–2950 cm^{-1} typical for valence oscillations of the CH bonds in the CH_2 groups of ethylenic bridges. In the IR spectra one can also observe the absorption bands in the range 2160–2170 cm^{-1} characteristic for Si—H bonds.

In the ^1H NMR spectra of copolymer IV one can observe a singlet signal with chemical shift of $\delta = 0, 35$ ppm., characteristic for group in —CH_2—CH_2—. In ^1H NMR spectra one can also observe signal with chemical shift with center at $\delta = 1{,}05$ ppm which may be assigned to methyl proton in the grouping >CH—CH_3, whose amount is about ~6%. This showed that the hydrid polyaddtion of α,ω-dihydriddimethylsiloxanes to 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane partially proceeds by Markovnikov scheme. One can observe also a singlet signal for Si—H protons. with chemical shift $\delta = 4, 8$ ppm.

On Figure 3 is presented the direct dependence of the recifrocal of concentration of the reactant on time. One can see, that the hydrid polyaddition reaction is the reaction of second order. From the Figure 3 the reaction rate constants at various temperatures were calculated: $K_{90°C} = 3{,}0797 \times 10^{-2}$, $K_{85°C} = 2{,}3007 \times 10^{-2}$ and $K_{80°C} = 1{,}6781 \times 10^{-2}$. Figure 4 shows the dependence of logarithm of the reaction rate constants on the reciprocal of temperature. From these data, the

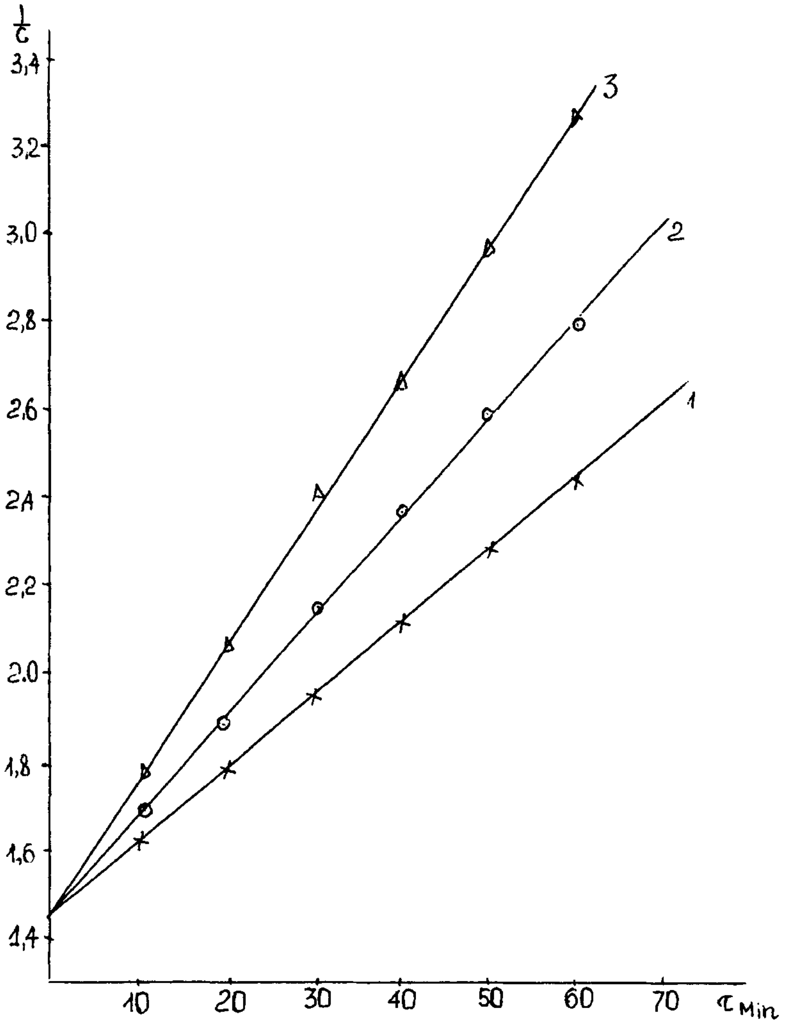


FIGURE 3 Dependence of reverse concentration on the time, where curve 1 is at 80°C curve 2 is at 85°C and curve 3 is at 90°C.

activation energy of the hydrid polyaddition reaction was calculated to be equal $E = 66{,}7$ KJ/mole. With the same values (62, 1KJ/mole) are characterized the hydrid polyaddition reaction of α,ω-dihydriddimethylsiloxanes to 1,5-divinyl-1,5-dimethylhexaphenylcyclopentasi-

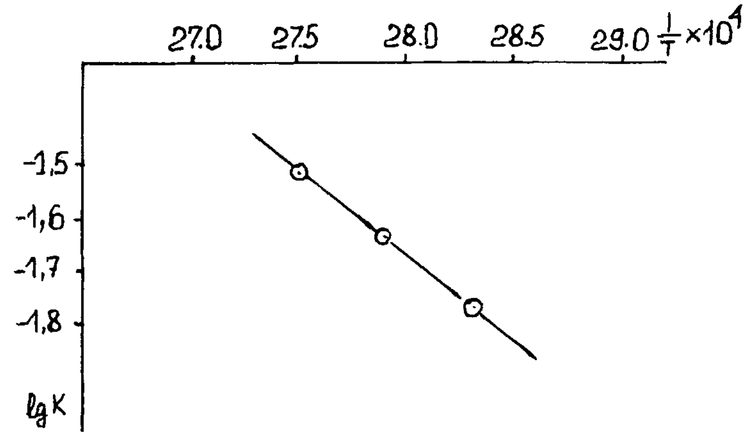


FIGURE 4 Dependence of reverse temperature on the logarithm of the rate constants of hydrid polyaddition reaction.

loxane [13]. A small difference (4,6 KJ/mole) may be explained by the steric effects, which create the cyclohexasiloxane fragments.

The thermogravimetric investigations of copolymers were carried out. As it is shown in Figure 5, 5% mass losses are observed in temperature interval 260–280°C. The main destruction process proceeds in the range 370–650°C. Above 700°C the curves of mass losses do not change. With an increase of the length of the linear PDMS links the mass losses increases and for copolymer III the residual mass consists of ~26% for copolymer VII–18%. The synthesized carbosiloxane copolymers containing cyclohexasiloxane fragments in the chain are characterized by lower thermal-oxidative stability than carbosiloxane copolymers containing cyclopentasiloxane fragments in the chain [13]. It is known that polymers with disiloethylene groups have lower thermal-oxidative stability, but higher thermal stability in the absence of oxygen in comparison with their polyorganosiloxane analogues.

With an increase of the volume of cyclic fragments the thermal-oxidative stability of copolymers decreases, which may be explained by the possibility of existence of $d_\pi - P_\pi$ conjugation in small cyclic fragments, which may increase their thermal-oxidative stability. These is in agreement with early opinion [14].

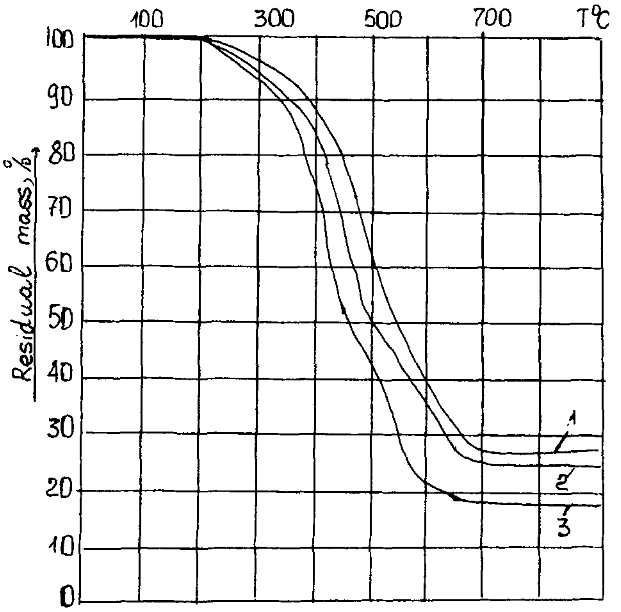


FIGURE 5 Thermogravimetric curves of cyclolinear carbosiloxane copolymers, where curve 1 is for copolymer III, curve 2 is for copolymer VII.

The roentgenographic investigations of synthesized copolymers were carried out. As it is seen from the amorpus copolymers diffractograms (Fig. 6), the copolymers are one phase systems. At small values of the length of the linear dimethylsiloxane links the interchain distance reached its maximum value $d_1 = 9{,}31$ Å (copolymer III). This value of d_1 is near to interchain distance of cyclohexasiloxane containing cyclolinear copolymers [15] and exceeding the value of interchain distances of cyclopentasiloxane containing carbosiloxane copolymers [13]. With an increase of the length of dimethylsiloxane links the interchain distances of copolymers decrease and for copolymer VII amounts to $d_1 = 7{,}24$ Å.

The thermomechanical investigations were also carried out with, synthesized copolymers. It was established that with an increase of the length of dimethylsiloxane links beginning from $n = 12$ the influence of cyclohexasiloxane fragments on the dimethylsiloxane chain is inperceptible. From the value of $n = 23$ copolymer VII the vitrification

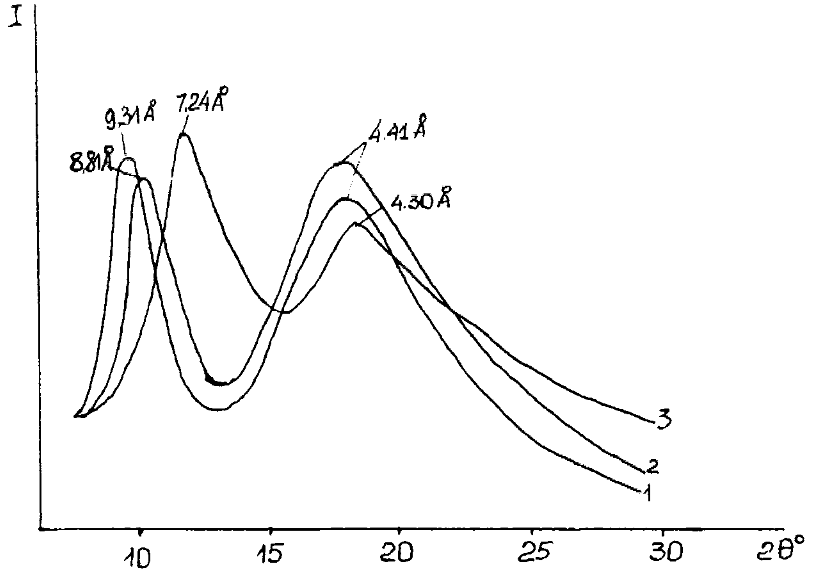


FIGURE 6 Diffractograms of copolymers, where curve 1 is for copolymer III, curve 2 is for copolymer V and curve 3 is for copolymer VII.

temperature of copolymer equal the vitrification temperature of PDMS. The vitrification temperature of synthesized copolymers are about ~15–20°C lower than their corresponding siloxane copolymers with cyclohexasiloxane fragments in dimethylsiloxane chain, at the same values of the length of dimethylsiloxane links. Heating of reprecipitated polymers at 100–110°C in the presence of 0,01–0,01 wt % catalysts of anionic polymerization there occurs an abrupt increase of viscosity and gel formation without giving of gas products. Changing the length of alkylsiloxane links between organocyclohexasiloxane fragments in the chain one can change the average distance between the cross-link sites.

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