CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2024,
Vol. 18, No. 2, pp. 131–142

Chemistry

CYCLIC SILICON ORGANIC COPOLYMERS: SYNTHESIS AND INVESTIGATION. REVIEW

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https://doi.org/10.23939/chcht18.02.131

Abstract. This paper considers the synthesis and investigation of cyclic silicon-organic polymers with mono- and polycyclic fragments in the side chain. For obtaining monocyclic polymers, the hydrosilylation reaction of 1-hydro-3-vinylhexamethylcyclotetrasiloxane was used. The reaction was conducted in a CCl_4 solution at 75 °C in the presence of Speier's catalyst ($H_2PtCl_6 \cdot 6H_2O$) to produce a viscous-flow at room temperature polymer. The polymers were studied by NMR spectroscopy. Poly(carbosiloxane) with cyclic fragments in the methyl-siloxane backbone was synthesized by the hydride polyaddition of divinylorganocyclosiloxane with dihydrodimethylsiloxane. A semi-quantitative assessment conducted using NMR spectroscopy revealed the ratio of isomeric 1,3- and 1,5-cyclic structures as 1:1. X-ray diffraction studies indicated that copolymers are single-phase amorphous systems. Also, in the review, synthesis and studies of carbosiloxane copolymers containing flexible dimethylsiloxane and decaorganotricyclodecasiloxane fragments in the backbone are discussed. Hydride polyaddition of divinyl-containing compounds was carried out for α,ω-dihydridedimethylsiloxanes of various lengths. The synthesized copolymers were characterized by the X-ray diffraction method and TGA.

Keywords: silicon-organic polymers; hydrosilylation; Speier's catalyst; carbosiloxane copolymers.

1. Introduction

Nowadays, the hydride polyaddition reactions are widely used in silicon organic chemistry. Recently, they have gained importance in obtaining complex monomers[1] and investigating the mechanisms and additions to various catalyst systems such as Pt, Pd, Co, and carbonyl metals. It is important to note the specificity of various catalytic systems[2–5].

According to the literature, dimethylsiloxane polymers' spiral-shaped structure varies when cyclic fragments are incorporated into the chain, which alters the polymers' physical and chemical characteristics[6].

To improve the thermal-oxidative stability of silicon-organic polymers, it is important to consider the synthesis method of functional groups containing organocyclosiloxanes and the modification methods of linear siloxane chains using reactions of hydride polyaddition to incorporate single or condensed cyclic fragments.

In addition to the hetero-functional condensation (HFC) reaction of preliminarily prepared cyclic organosiloxanes with functional groups and difunctional organosilicon compounds, which allows for the preservation of cyclic groups in the polymeric backbone, hydride polyaddition is also widely used. This process occurs under soft conditions, without the elimination of by-products, and does not involve the breaking cyclic structures that have been introduced into the backbone[7–9].

The synthesized carbosiloxane copolymers with disilylethylene groups in the main chain possess less thermal-oxidative stability in comparison with polyorganosiloxane analogs, but they have greater thermal stability in the absence of oxygen.[9]

This paper reviews the synthesis and investigation of cyclolinear carbosiloxane copolymers with regular arrangement of mono-, bi- and tricyclic fragments in a dimethylsiloxane backbone using the hydride polyaddition reaction as a method for polymer synthesis.

2. Carbon Siloxane Polymers with Monocyclic Fragments in the Main Chain: Synthesis and Investigation

The first cyclolinear organosiloxane polymers with ethylene bridges between cyclosiloxane rings were synthesized by hydrosilylation reaction 1-hydro-3-vinylhexamethylcyclotetrasiloxane. The starting compound 1-

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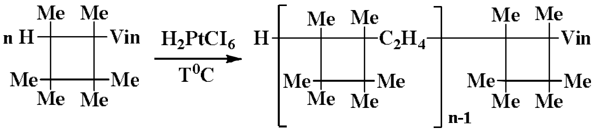
hydro-3-vinylhexamethylcyclotetrasiloxane was synthesized by co-hydrolytic condensation of symmetric tetramethyldichlorosilane with 1,3-dichloro-1,3-dimethyl-3-vinyldisiloxane. The yield for obtained 1-hydro-3-vinylhexamethylcyclotetrasiloxane was about 67 %. Hydrosilylation reaction for 1-hydro-3-vinylhexamethylcyclotetrasiloxane was performed in CCl_4 solution medium at 75 °C in the presence of Speier's catalyst (H_2PtCl_6 x $6H_2O$), and viscous-flow at room temperature polymer, has been synthesized by the following Scheme 1[10].



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Scheme 1. Hydrosilylation reaction of 1-hydro-3-vinylhexamethylcyclotetrasiloxane

Cyclolinear polymers are synthesized using tetrasiloxane rings as elementary units, which are bound together by ethylene bridges. It is found that hydrosilylation proceeds without breaking the cyclotetrasiloxane ring and a low-molecular polymer with a molecular mass M=2260 is synthesized in the reaction, well-soluble in benzene and other organic solvents. Besides the peak displayed by ≡Si-Me groups, the NMR spectrum possesses one non-splitter peak typical of $\equiv Si\text{-}CH_2$- groups with chemical shift (concerning ≡Si-Me groups) equal $\delta = 0.35$ ppm.

The polyhydrosilylation reaction's kinetic characteristics were studied by reducing the quantity of active ≡Si-H bonds. The catalyst was tested at different temperatures and concentrations.

The integral absorption intensity of active γ(≡Si-H) bonds at 2160–2170 cm^{-1} was calculated spectroscopically for the kinetic calculation, where obtained results are reproducible. Moreover, the content of active ≡Si-H groups was determined by the chemical method.

Table 1 presents the reaction rate constants for the hydrosilylation reaction, which has been determined to be a second-order reaction based on the calculations. The values were calculated for different temperatures and catalyst amounts.

Table 1. The reaction rate constants at different temperatures and catalyst amounts for hydrosilylation reaction of 1-hydro-3-vinylhexamethylcyclotetrasiloxane

No.	Concentration of catalyst $H_2PtCl_6 \times H_2O$	$K \times 10^{-3}$			
		50^0	65^0	75^0	85^0
1	1.4	0.675	1.72	5.7	7.8
2	2.1	1.76	–	9.45	–
3	2.8	3.59	–	13.75	–

The study investigated the relationship between the logarithm and the rate constants at different temperatures, with a catalyst concentration of approximately $C \approx 1.4 \times 10^{-4}$ mol/L from which the activation energy of a hydrosilylation reaction equals E=17.0 kcal/mol. Arrhenius factor $A = 2.9 \times 10^8$ L/mol·sec was calculated.

As demonstrated by the experiment the hydrosilylation rate constants at 50 °C and 75 °C exhibit a linear dependence on a catalyst concentration. The dependence presented is linear, indicating that the hydrosilylation of 1-hydro-3-vinylhexamethylcyclotetrasiloxane occurs through the formation of a transition complex between the initial monomer and the catalyst. The hydrosilylation proceeds under the first order from a catalyst concentration.

Poly(carbosiloxane) with cyclic tetrasiloxane fragments in the methyl-siloxane backbone was synthesized by the hydride polyaddition of divinylorganocyclosiloxane by dihydrodimethylsiloxane[11]. The polymers were synthesized in an argon environment using a 1:1 molar ratio of the initial reagents. No diluter or inert organic solvent, such as toluene, was present during the synthesis process. The synthesis took place at a temperature range of 100–110 °C.

Platinum hydrochloric acid was added to the reaction mixture as a catalyst. The amount used was $1 \div 1.5 \times 10^{-5}$ g of $H_2PtCl_6 \times 6H_2O$ per 1 g for the initial mixture.

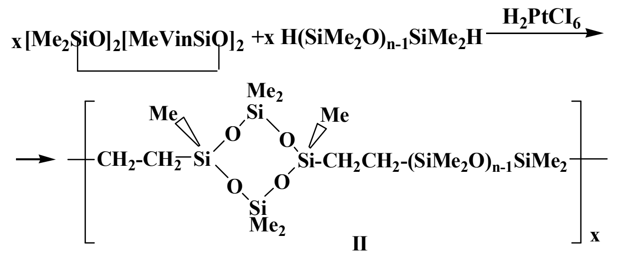
Half of the amount was added before the reaction initiation, and the second half was 25÷140 hours after the beginning of heating. Platinum hydrochloric acid was added in the form of 0.01 M solution in tetrahydrofuran. Isopropyl alcohol was used as a diluent for $H_2PtCl_6 \times 6H_2O$ resulting in a decrease in the relative viscosity of the synthesized polymers. This decrease may be attributed to the side alkoxylation reaction (Scheme 2).

$$\equiv Si{-}H + HO{-}C_3H_7 \xrightarrow{Cat} \equiv Si{-}O{-}C_3H_7 + H_2$$

Scheme 2. Dehydrocondensation reaction of ≡Si-H bond and isopropyl alcohol

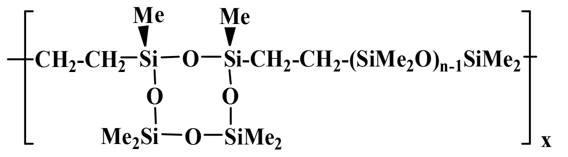
Linear poly(organocarbosiloxanes) with cyclic structures in the backbone were synthesized by the following Scheme 3[11].

Synthesized polymers represent viscous and highly viscous colorless transparent liquids, soluble in cyclic hydrocarbons and lower esters. The inherent viscosity of the derived polymer is not significantly affected by the reaction taking place in an inert organic solvent, such as toluene. Synthesis of polymers with high viscosity in the presence of a solvent can be achieved by longer heating of the reaction mixture. From the authors' point of view, polymers with cyclic fragments in the backbone are interesting due to their high reactivity. For example, these polymers can readily create crosslinked structures in anionic catalysts. Initial divinylhexamethylcyclotetrasiloxane was synthesized by combined hydrolysis of dimethyldichlorosilane and methylvinyldichlorosilane.



Scheme 3. Hydrosilylation reaction α,ω-dihydridedimethylsiloxanes to divinylorganocyclotetrasiloxanes, where $n = 0, 1, 4, 5, 6, 10, 20, 27, 34, 57, 94, 150, 200$

Although the authors applied efficient rectification columns and an analytical chromatograph with a preparative add-on device, they were unable to separate isomeric 1,3- and 1,5-divinylhexamethylcyclotetrasiloxanes, which may be formed in the cooperative hydrolysis. That is why isomeric structural groups as follows (III) may also be present in synthesized polymers (Scheme 4).



III

Scheme 4. Carbosiloxane cyclolinear organosiloxane copolymers with 1,3-arrangement of hexamethylcyclotetrasiloxane fragment in a dimethylsiloxane chain

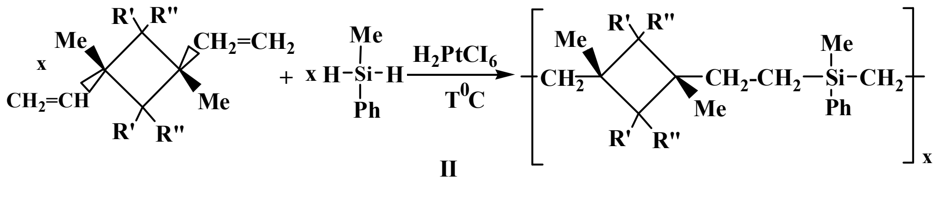
A semi-quantitative assessment was performed using NMR spectra to determine the ratio of isomeric 1,3- and 1,5-cyclic structures in synthesized polymers. The results showed a 1:1 ratio.

The study analyzed variations in the content of functional groups (≡Si-H, as determined by IR-spectroscopy) and the increase in specific viscosity of the reaction mixture during the reaction process. The polymers' maximum viscosities ([η] = 0.17–0.97 dL/g) were observed after 50–160 hours of heating. In most cases, the maximum viscosities were dependent on the length of the α, ω-dihydropolydimethylsiloxane chain and the purity of the initial compounds used.

The IR spectra of the synthesized poly(organocyclocarbosiloxanes) suggest that the polymers are synthesized due to hydride polyaddition, preserving the structures of the initial compounds rather than polymerizing the cyclic hexamethyldivinylcyclotetrasiloxane. Preliminary experiments on the long-term heating of the mixture of initial hexamethyldivinylcyclotetrasiloxane isomers under polyaddition conditions support this conclusion.

The organocyclotetrasiloxanes fragment presence in the structure of synthesized poly(organocyclocarbosiloxanes) may be proved by their transition into a non-fusible, insoluble state due to polymerization of organosiloxane cycles existing in the polymer structure. As reprecipitated polymers are heated at 100–110 °C in the presence of 0.001–0.01 wt. % of anionic polymerization catalysts, viscosity is considerably increased and gel is formed. Varying length of alkylenesiloxane bridge between organocyclotetrasiloxanes fragments of poly(organocyclocarbosiloxanes) backbone, one may change the average distance between cross-link points and, consequently, properties of cross-linked polymers formed.

Hydride polyaddition between 1,5-divinyl-1,5-dimethyl-3,3,7,7-tetraorganocyclotetrasiloxane and methylphenylsilane has been studied[12]. All attempts to separate initial divinylorganocyclotetrasiloxanes into *cis*- and *trans*-isomers have failed. Based on NMR data, the initial divinylorganocyclotetrasiloxanes are a mixture of *cis*- and *trans*-isomers. The reaction proceeds according to Scheme 5.

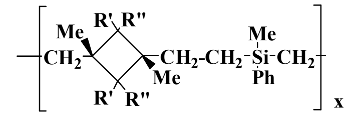


Scheme 5. The catalytic hydrosilylation reaction of α,ω-dihydridephenylmethylsilane and 1,5-divinyl-1,5-dimethylorganocyclotetrasiloxanes, where R′ = Me; R″ = Ph; R′ ≠ R″

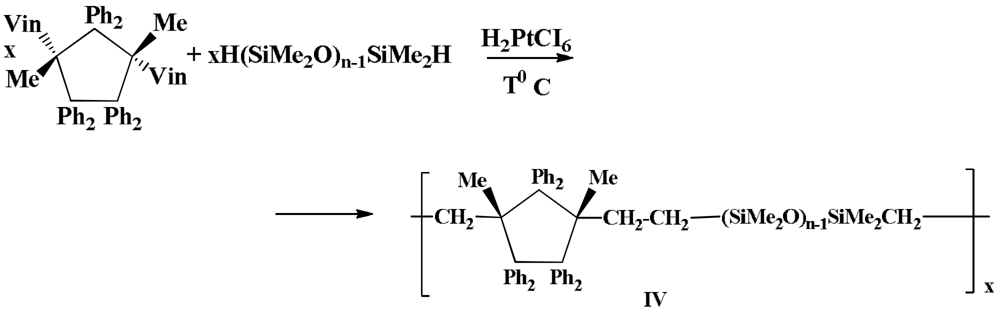
Polyaddition reaction was carried out at 60–70 °C, and at the final stage, the mixture was heated up to 100 °C. The catalyst in the amount of 5×10^{-4} mol Pt/mol was added to vinylcyclosiloxane, and heated up to 50 °C. Some parameters of synthesized copolymers are shown in Table 2.

To synthesize carbosiloxane copolymers with organocyclopentasiloxane fragments in the dimethylsiloxane backbone, we studied the hydride polyaddition reaction among α,ω-dihydridedimethylsiloxanes and 1,5-divinyl-1,5-dimethylhexaphenylcyclopentasiloxane using platinum hydrochloric acid as a catalyst. The reaction was conducted at temperatures below 100 °C, specifically at 75 °C, 80 °C, and 85 °C. The initial 1,5-divinyl-1,5-dimethylhexaphenylcyclopentasiloxane is a mixture of *cis-* and *trans-*isomers. Copolymers derived from them are atactic. Preliminary heating of the initial compounds in the presence of the catalyst at a temperature range of 80–95 °C showed that organocyclopentasiloxane fragments do not polymerize under these conditions.

Table 2. Physical and chemical parameters of cyclolinear poly(organocarbosiloxane) copolymers

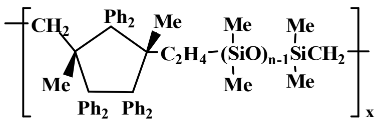
No.	Copolymer	*R′*	*R″*	[η], dl/g	T_{degr}*, of 5 % mass Loss	Coke residue, (800 °C), %	T_g, °C
1		Me	Me	0.08	240	52	-7
2		Me	Ph	0.06	320	45	26
3		Ph	Ph	0.04	370	41	13

* TGA data for polymers treated by heptamethylvinylcyclotetrasiloxane.



Scheme 6. The catalytic hydrosilylation reaction of α,ω-dihydridedimethylsiloxanes and 1,5-divinyl-1,5-dimethylhexaphenylcyclopentasiloxanes, where: $n = 2 \div 23$

Table 3. Physical and chemical parameters of carbosiloxane copolymers containing cyclopentasiloxane fragments (structure III)

No.	Copolymer	n_{SiO}	Yield, %	Reaction T,^{0}C	η^*_{sp}	T_g, ^{0}C	d_1, Å	5 % mass losses	$\overline{M}_\omega \times 10^{-3}$
1		2	75	85	0.09	0÷–2	9.20	320	189
2		4	80	85	0.14	–22	–	–	–
3		6	92	75	0.15	–	–	–	–
3′		6	93	80	0.18	–	–	–	–
3″		6	95	85	0.20	–53	–	295	211
4		12	95	85	0.24	–82	–	–	–
5		23	96	85	0.31	–123	7.21	285	236

* In toluene at 25 ^{0}C.

Synthesized copolymer structure was determined using ^{29}Si NMR spectral data. The reaction progress was monitored by observing a decrease in the amount of active ≡Si-H groups. It was observed that the rate and depth of polyaddition reaction decrease with an increase in the chain length of α,ω-dihydridedimethylsiloxanes. The hydride polyaddition proceeds according to Scheme 6[2, 13].

As a result of the reaction, copolymers with η_{spec} = 0.09–0.26 are obtained, which are liquid or glassy light-yellow products, soluble in ordinary organic solvents. Some physical and chemical parameters, as well as the yield of copolymers are listed in Table 3.

In the case of short lengths of the dimethylsiloxane backbone, *n*, the copolymer's yield is low. This may be explained by the fact that besides intermolecular reaction, intramolecular cyclization proceeds to form a polycyclic structure. This conclusion is in agreement with data from the literature[13–18].

The amount of active ≡Si-H groups was reduced as the hydride polyaddition proceeded. Figure 1 shows that the rate of hydride polyaddition increases with temperature (at the same values of dimethylsiloxane units, *n*), but on the other hand, with an increase in the length of dimethylsiloxane links (*n*) at the same temperatures, the rate of hydride polyaddition decreases. Fig. 1 shows that the conversion of active ≡Si-H groups is not complete and decreases from 20 % (*n* = 6) to 15 % (*n* = 12).

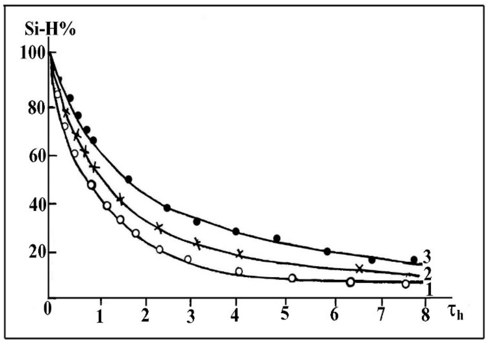
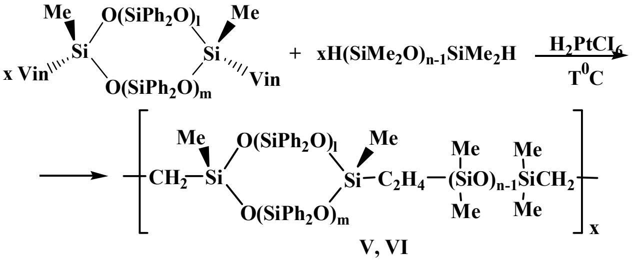


Fig. 1. Time dependence of changes in active ≡Si-H % groups during polyaddition of α, ω-dihydridedimethylsiloxane (*n* = 6) with 1,5-divinyl-1,5-dimethylhexaphenylcyclo-pentasiloxane: 1 – at 85 °C; 2 – at 80 °C and 3 – at 75 °C

Polyaddition was found to be a second-order reaction. The reaction rate constants and the activation energy were calculated: k_{75^oC}=1.4004×10^{-2}, k_{80^oC}=1.965×10^{-2}, k_{85^oC}=2.559×10^{-2} L/mol·s; E_{act}=62.1 kJ/mol, respectively.

^{1}H NMR spectra of copolymers indicate that catalytic hydride polyaddition mainly proceeds by the Farmer rule with the formation of dimethylenic bridges. In these spectra a reflex of $-CH_2-CH_2-$ group with a chemical shift δ=0.34 ppm is observed; it is indicated that hydride polyaddition partly (about 6–7 %) proceeds by the Markovnikov rule.

Cyclolinear carbosiloxane copolymers with 1,7- and 1,5-disposition of dimethyloctaphenylcyclohexasiloxane fragments in the dimethylsiloxane backbone were synthesized by the hydride polyaddition of α,ω-dihydridedimethylsiloxane to 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane and 1,5-divinyl-1,5-dimethyloctaphenylcyclohexasiloxane in the presence of a catalyst. Polyaddition reactions were studied below 100 °C. It was also indicated that under these conditions polymerization or polycondensation of initial compounds does not take place. Polyaddition proceeds according to Scheme 7[19–21].



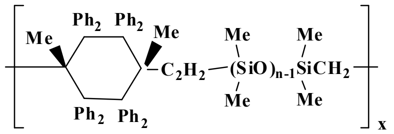
Scheme 7. The catalytic hydrosilylation reaction of α,ω-dihydridedimethylsiloxane and 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane (1,5-divinyl-1,5-dimethyloctaphenylcyclohexasiloxane),
where: $m = l = 2$ (IV); $n = 2 \div 23$; $l = 1$, $m = 3$ (V); $n = 2$–23

Since 1,7- and 1,5-divinylcyclohexasiloxanes, used in polyaddition, represent mixtures of *cis*- and *trans*-isomers of the approximate 52:48 ratio, the synthesized copolymers are atactic. Re-precipitation of copolymers from the toluene solution by methyl alcohol has given viscous or solid (concerning the value of flexible junction) transparent products with η_{spec}=0.09–0.29, well soluble in different organic solvents. It is found that at a short length of dimethylsiloxane unit ($n \leq 4$), copolymer yields are slightly decreased which may be explained by the partial proceeding of hydride polyaddition by intramolecular cyclization mechanism (see Tables 4 and 5).

After solvent removal from the mother solution of re-precipitated copolymer 1 (Table 4), a semicrystalline compound with a molecular mass equal to ~1100 was obtained[20,21]. Only the product with the structure resulting from the intramolecular cyclization of 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane and 1,3-dihydride-tetra-methyldisiloxane can exhibit the current molecular mass. The macromolecular chain is formed with the participation of divinylorganocyclohexasiloxane. The structure and composition of the synthesized cyclolinearcarbosiloxane copolymers were determined through functional and ultimate analysis, as well as IR and NMR spectral data. Some parameters of copolymers are shown in Tables 4 and 5.

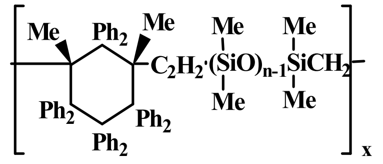
A reflex with the chemical shift at δ=0.35 ppm typical of $-CH_2-CH_2-$group is observed in ^{1}H NMR spectrum of copolymer 1 (Table 4). This indicates that the polyaddition proceeds under the Farmer's rule. A duplet centered at δ=1.06 ppm, corresponding to methyl protons in $=CH-CH_3$ group, is also observed in the spectrum. Based on the ratio of intensities, it was concluded[19, 20] that the polyaddition partly proceeds by the Markovnikov mechanism (6–8 %). The spectra show a complex multiplet with a chemical shift at δ=5.6–6.2 ppm, characteristic of vinyl protons that do not participate in the polyaddition reaction, and a singlet for ≡Si-H protons with a chemical shift at δ=4.4 ppm, which also do not participate in the reaction.

Table 4. Physical and chemical parameters of carbosiloxane copolymers with 1,7-disposition of cyclic hexasiloxane fragments in the dimethylsiloxane backbone

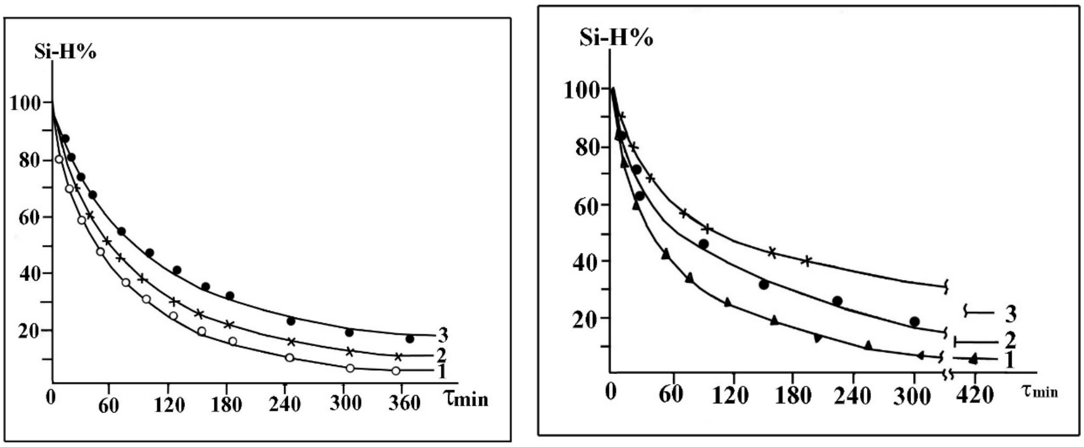
No.	Copolymer V	n_{SiO}	Yield, %	Reaction T,⁰C	η^*_{sp}	T_g, ⁰C	d_1, Å	5 % mass losses	$\overline{M}_\omega \times 10^{-3}$
1		2	74	90	0.10	+5	9.31	280	174
2		4	80	90	0.12	–10	–	–	–
3		6	94	80	0.17	–	–	–	–
3′		6	94	80	0.17	–	–	–	–
3″		6	95	85	0.18	–40	8.81	280	194
4		12	96	90	0.23	–68	8.40	–	–
5		23	95	90	0.29	–123	7.24	260	231

* In toluene at 25 °C.

Table 5. Physical and chemical parameters of carbosiloxane copolymers with 1,5-position of cyclic hexasiloxane fragments in the dimethylsiloxane backbone

No.	Copolymer VI	n_{SiO}	Yield, %	Reaction T,⁰C	η^*_{sp}	T_g, ⁰C	d_1, Å	5 % mass losses	$\overline{M}_\omega \times 10^{-3}$
1		2	72	10	0.09	+8	9.60	270	159
2		4	84	85	0.11	–12	–	–	–
3		6	86	80	0.15	–	–	–	–
3′		6	89	90	0.18	–	–	–	–
3″		6	94	100	0.15	–38	8.90	265	180
4		12	95	100	0.22	–72	8.34	–	210
5		23	95	100	0.28	–123	–	260	–

* In toluene at 25 °C.



(A) (B)

Fig. 2. **(A)** Decrease of ≡Si-H bond concentration during hydride polyaddition of α, ω–dihydridedimethylsiloxane (n = 6) to 1,7-divinyl-1,7-dimethyloctaphe-nylcyclohexasiloxane: 1 – 90 °C; 2 – 85 °C; 3 – 80 °C. **(B)** Decrease of ≡Si-H bond concentration during hydride polyaddition of α, ω-dihydridedimethylsiloxane (n = 6) to 1,5-divinyl-1,5-dimethyloctaphenyl cyclohexasiloxane: 1 – 100 °C; 2 – 90 °C; 3 – 80 °C

Hydride polyaddition proceeded at different temperatures. Figs. 2 and 3 show variations of ≡Si-H bond concentration during polyaddition of α, ω-dihydridedimethylsiloxane ($n = 6$) to 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane and 1,5-divinyl-1,5-dimethyloctaphenylcyclohexasiloxane. It is observed that hydride polyaddition depth is increased with the reaction temperature. Moreover, the effect of 1,7- or 1,5-disposition of vinyl groups in cyclohexasiloxane fragments is the negligible factor for their reactivity.

It is found that in the initial stages, the polyaddition is a second-order reaction. In the case of 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane, the polyaddition rate constants for different temperatures were determined as follows: $k_{90^oC}=3.0797\times10^{-2}$; $k_{85^oC}=2.3007\times10^{-2}$; $k_{80^oC}=1.6781\times10^{-2}$ L/mol·s. Activation energies for 1,7-divinyl-1,7-dimethyloctaphenylcyclohexasiloxane and 1,5-divinyl-1,5-dimethyl-octaphenylcyclohexasiloxane were also calculated: $E_{act}=66.7$ and $E_{act}=69.7$ kJ/mol, respectively. These values are very close.

X-ray diffraction studies have indicated that copolymers are single-phase amorphous systems, and maximal interchain distance is observed for short dimethylsiloxane unit length ($n = 2$); hence, for copolymer 1 (Table 4), d_1 = 9.60 Å. This value is slightly greater than the interchain distance of carbosiloxane copolymer 1 (Table 3) with 1,7-disposition of cyclohexasiloxane fragment in the dimethylsiloxane backbone (n=2). As a flexible junction length is increased, d_1 decreases and approaches the interchain distance in PDMS; it increases with the volume of cyclic fragment at the same lengths of flexible dimethylsiloxane unit, i. e. at the transition from Cyclopentasiloxane to cyclohexasiloxane fragment.

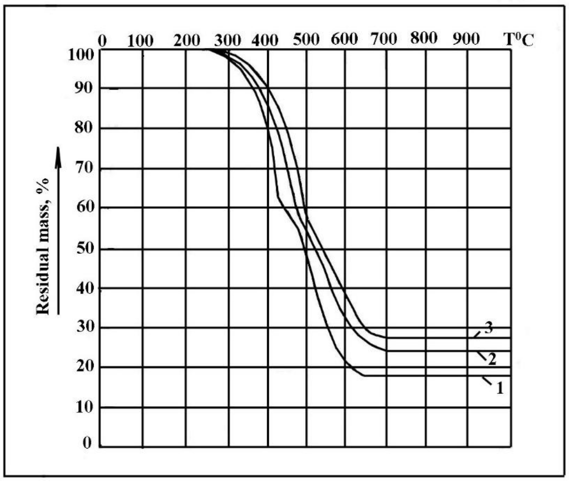


Fig. 3. Thermogravimetric curves of carbosiloxane copolymers: 1 – copolymer 4 (Table 4) with 1,5-disposition of cyclic hexasiloxane fragment in the backbone; 2 – co-polymer 1 (Table 3) with 1,7-disposition of cyclic hexasiloxane fragment in the back-bone; 3 – copolymer 1 (Table 2) with cyclic pentasiloxane fragment in the backbone

Thermogravimetric studies of carbosiloxane copolymers have indicated a 5 % mass loss of the compounds in the temperature range of 250–260 °C. The main degradation process proceeds in the range of 380–630 °C, and above 700 °C the mass loss is not observed. It is found that the thermal oxidative stability of copolymers decreases with an increasing cyclic fragment volume, *i. e.* at the transition from cyclic pentasiloxane to hexasiloxane fragments in cyclolinear carbosiloxane copolymers. It is also found that carbosiloxane copolymers with 1,7- and 1,5-disposition of cyclic hexasiloxane fragments in the backbone are characterized by almost identical thermal oxidative stability.

Therefore, it was concluded[20, 21] that the thermal oxidative stability of carbosiloxane copolymers is not significantly affected by the 1,7- or 1,5-disposition of the cyclic hexasiloxane fragment (as shown in Fig. 3). On the other hand, compared with pure siloxane analogues, the thermal oxidative stability of carbosiloxane copolymers is lower.

Thermogravimetric studies have demonstrated that the cyclic fragment has a significant impact on carbosiloxane copolymer only at n=12. At n≈23, no effect of the cyclic fragment on the copolymer's glass transition temperature is observed. Fig. 4 shows the dependence of T_g on the length of dimethylsiloxane unit for cyclolinear carbosiloxane copolymers.

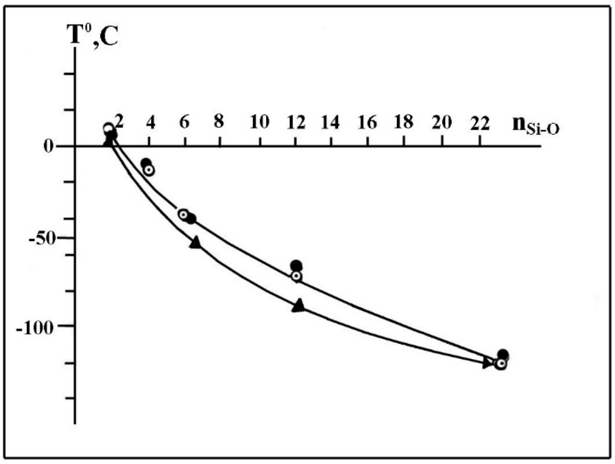


Fig. 4. Dependence of T_g for cyclolinear carbosiloxane copolymers on the length of dimethylsiloxane unit: 1 – copolymer with 1,7-position of cyclic hexasiloxane fragment; 2 – copolymer with 1,5-position of cyclic hexasiloxane fragment

It has been found that increasing the volume of the cyclic fragment for the same length of dimethylsiloxane unit, *i. e.* introducing a single diphenylsiloxane unit, increases the T_g of the copolymer by ~10 °C. It is also shown that the effect of 1,7- or 1,5-disposition of cyclic hexasiloxane fragment on T_g of the copolymer is negligible, which conforms to the previous results on pure siloxane copolymers[22].

3. Carbosiloxanes with Tricyclic Fragments in the Backbone

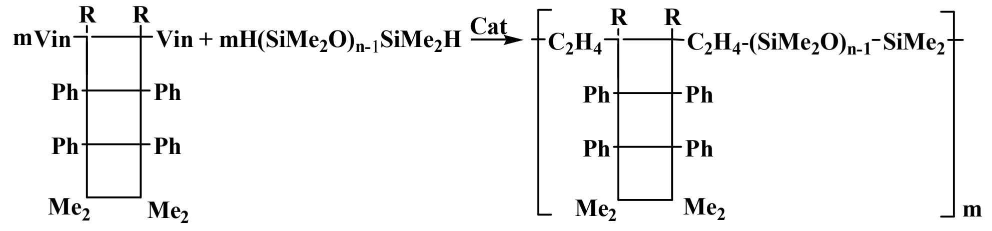
The present chapter discusses synthesis and studies of carbosiloxane copolymers containing flexible dimethylsiloxane and decaorganotricyclodecasiloxane fragments in the backbone[23,24]. To synthesize carbosiloxane copolymers, hydride addition of α,ω-dihydridedimethylsiloxane to 1,3-divinyl-1,3,9,9,11,11-hexamethyl-5,7,13,15-tetraphenyltricyclodecasiloxane was performed at a temperature below 90 °C. Therefore, cyclosiloxane ring disclosure did not take place under conditions of hydride polyaddition.

Preliminary heating of initial divinylorganotricyclodecasiloxane for 10 hours at a temperature of 70–90 °C in the presence of rhodium acetylacetonate dicarbonyl or platinum hydrochloric acid as a catalyst did not initiate polymerization of the primary divinyltricyclodecasiloxane. Thorough analysis of the reaction mixture by a gas liquid chromatography method has detected the presence of initial organosiloxanes. Besides, there are no changes in the NMR and IR spectra of divinyl-containing compounds and dihydridedimethylsiloxanes.

Hydride polyaddition of divinyl-containing compounds was carried out for various lengths of α,ω-dihydridedimethylsiloxanes. The reaction run was searched by a decrease in active ≡Si-H groups' concentration. It was found that for rhodium acetylacetonate dicarbonyl as a catalyst, copolymers soluble in organic solvents were obtained, which were structured after some time. This may be explained by the fact that despite polymers re-precipitated from the toluene solution by a methyl alcohol, the rhodium catalyst remains in polymeric systems, which decompose and induce structuring (crosslinking) of copolymers.

Therefore, copolymers were synthesized in the presence of platinum hydrochloric acid as the catalyst. The rate and depth of polyaddition are decreased with the increase of α,ω-dihydride-dimethylsiloxane chain length. Fig. 5 shows that conversion of ≡Si-H bond is incomplete and decreases from 95 % (n = 4) to 83 % (n = 12).

Hydride polyaddition of α,ω-dihydridedimethylsiloxane to divinylorganotricyclodecasiloxane proceeds according to Scheme 8[23,24].



VII

Scheme 8. The catalytic hydride addition reaction of α,ω-dihydridedimethylsiloxane and 1,3-divinyl-1,3,9,9,11,11-hexamethyl-5,7,13,15-tetraphenyltricyclodecasiloxane, where n=2 ÷21; Cat is H_2PtCl_6

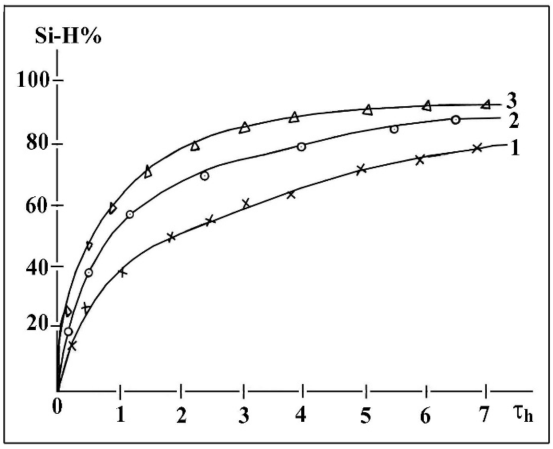
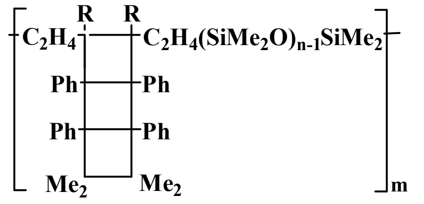


Fig. 5. Time dependence of ≡Si-H group concentration (%) on polyaddition of α,ω-dihydridedimethylsiloxane to divinylorganotricyclodecasiloxane at 90°C for dimethylsiloxane backbone lengths: 1— n = 12; 2 – n = 6; 3 – n = 4

Table 6. Some physical and chemical parameters of carbosiloxane cyclolinear copolymers with tricyclodecasiloxane fragments in the backbone

No.	Copolymer structure VII	n_{SiO}	Yield, %	T_{react}, ^{0}C	η^*_{sp}	T_g, ^{0}C	d_1, Å	$\overline{M}_{\omega}\times10^{-3}$
1		2	80	90	0.08	–12	10.20	72
2		4	83	70	0.09	–	–	–
3		4	88	80	0.11	–	–	–
4		4	91	90	0.11	–50	–	85
5		6	92	90	0.14	–96	8.68	–
6		12	93	90	0.20	–123	–	–
7		21	94	90	0.26	–123	7.54	110

* In toluene at 25 °C; molecular masses were determined by the gel chromatography.

As a result of the reaction, the synthesized copolymers possess η_{spec}=0.08–0.26 and represent liquid or glassy-like light yellow transparent products, soluble in ordinary organic solvents. Some physical and chemical parameters, molecular weights, and yields of the synthesized copolymers are shown in Table 6.

The reaction proceeding was also monitored by the increase in the synthesized copolymer viscosity. It was found that viscosity of copolymers and the hydride polyaddition degree increase with the increase in temperature to 70–90 °C. The conversion of the ≡Si-H bond in the hydride polyaddition of α,ω-dihydridedimethylsiloxane to divinylorganotricyclodecasiloxane increases with the temperature from 85 % at 70 °C to 95 % at 90 °C. Fig. 7 illustrates the time dependence of the ≡Si-H concentration (%) decrease at different temperatures.

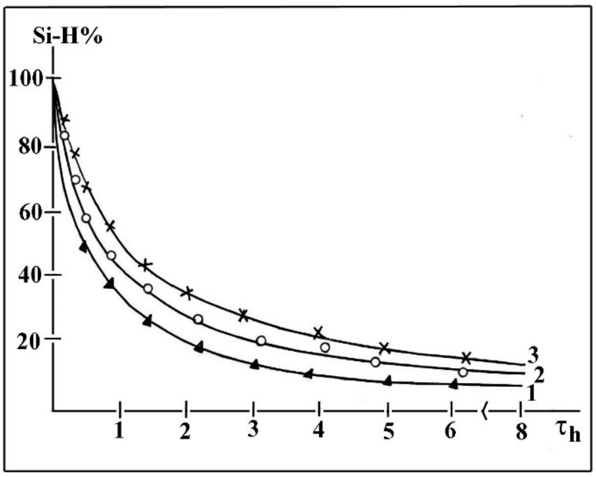


Fig. 6. Time dependence of ≡Si-H group concentration (%) on polyaddition of α,ω-dihydridedimethylsiloxane (n=4) to divinylorganotricyclodecasiloxane: 1 – 90 °C; 2 – 80 °C; 3 – 70 °C

Time dependence of reverse reagent concentration displays the second order of hydride polyaddition. Further on, reaction rate constants for various temperatures were calculated: $k_{70^0C}\approx1.1086\times10^{-2}$, $k_{80^0C}\approx1.6196\times10^{-2}$, $k_{90^0C}\approx2.3834\times10^{-2}$ L/mol·s. It was shown that the reaction rate constants increase by approximately 1.5 times for every 10°C of temperature rise. The activation energy of hydride polyaddition was derived from the dependence of the reaction rate constant logarithm on reverse temperature: E_{act}=64.4 kJ/mol.

The study of the ^{1}H NMR spectrum for copolymer 2 (Table 6) shows that the catalytic hydride polyaddition mainly occurs according to the Farmer's rule with the formation of dimethylene bridges. NMR spectrum also displays a reflex of -CH_2-CH_2- group with the chemical shift of δ=0.35 ppm. A duplet reflex centered at the chemical shift of δ=1.12 ppm, corresponded to methyl protons in =CH-CH_3 groups with 5–6% concentration was also observed. Integral ratios of methyl and phenyl protons correspond to the formula of copolymer 2 (Table 6).

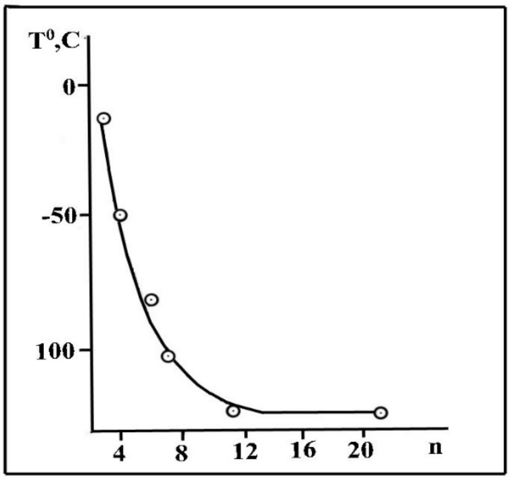


Fig. 7. T_g dependence of cyclolinear carbosiloxane copolymers (VI) on the length of linear poly(dimethylsiloxane), n

Thermomechanical studies of synthesized copolymers indicate that the glass transition temperature of copolymers is decreased with an increase in the linear dimethylsiloxane backbone length, *n* (Fig. 7). Since n=12 carbotricyclodecasiloxane fragments in copolymers cause no effect on the dimethylsiloxane backbone and T_g of copolymer 6 (Table 6) remains equal –123 °C.

Contrary to previous considerations[25], dimethylsiloxane backbone length increase (n=21) does not cause the formation of two-phase systems in cyclolinear copolymers with rigid decaphenyltricyclodecasiloxane fragments and flexible dimethylsiloxane units (n=25).

The copolymers containing carbotricyclodecasiloxane and tricyclodecasiloxane fragments were compared, and it was found that the former had lower glass transition temperatures. This could be due to the excessive concentration of flexible -CH_2-CH_2- groups in its backbone.

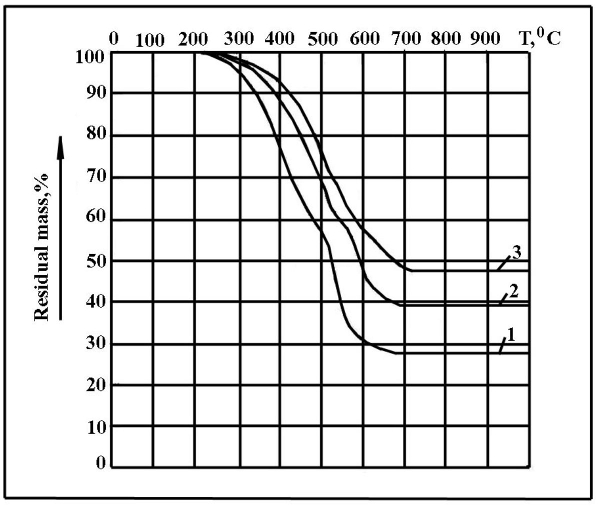


Fig. 8. Thermogravimetric curves of cyclolinear carbosiloxane copolymers: 1 – copolymer 7; 2 – copolymer 5; 3 – copolymer 1 (Table 6, in air, at 5 deg/min heating rate)

Thermogravimetric studies of copolymers show (Fig. 8) their higher thermal oxidative stability for a short length of the dimethylsiloxane backbone, *n*. As the length of dimethylsiloxane backbone increases, the thermal oxidative stability of copolymers decreases. Compared with siloxane analogies, the thermal oxidative stability of carbotricyclodecasiloxane-containing copolymers is lower[25]. In the temperature range of 300–350 °C mass losses of the polymer are below 3–7 %, and the main degradation process proceeds at 400–650 °C. Above 650 °C, the curves of mass losses are preserved unchanged (Fig. 8).

As carbotricyclodecasiloxane fragments are introduced into the dimethylsiloxane backbone, the main degradation process proceeds at a temperature of 80–100 °C higher than for unblocked poly(dimethyl-siloxane).

Synthesized copolymers were studied by the X-ray diffraction method. Diffraction patterns of amorphous polymers (Fig. 9) show that the interchain distance reaches its maximum (d_1=10.24 Å) at short lengths of flexible dimethylsiloxane backbone, *n*. As the length of dimethylsiloxane backbone increases (n=21), the interchain distance decreases and for copolymer 5 reaches 7.54 Å (Table 6).

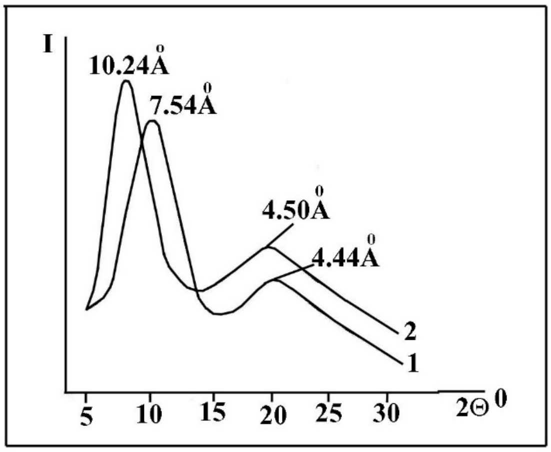
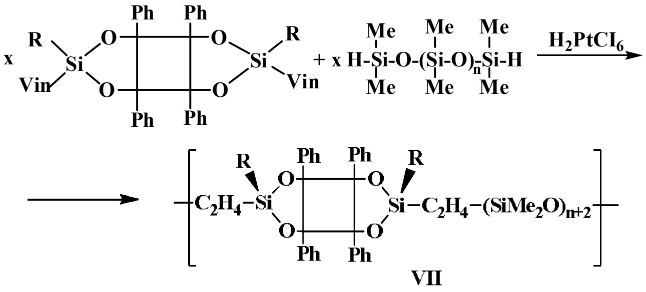


Fig. 9. Diffraction patterns of copolymers: 1 – copolymer 5; 2 – copolymer 1 (Table 6)

Thus copolymer 7 does not form a two-phase system, as observed for copolymers with decaphenyltricyclodecasiloxane fragments in the dimethylsiloxane backbone. This may be explained by the presence of the combination of rigid carbotricyclosiloxane and flexible dimethylsiloxane fragments in it. Therefore, copolymers represent single-phase systems.

To synthesize carbosiloxane copolymers with tricyclohexasiloxane fragments in the backbone, hydride polyaddition reaction of α,ω-dihydridepoly (dimethylsiloxanes) to 1,7-divinyl-1,7-dimethyl-3,5,9,11-tetraphenyl tricyclohexasiloxane was studied[26]. The reaction was implemented in anhydrous toluene in the presence of platinum-hydrochloric acid in tetrahydrofuran and the temperature range of 70–170 °C according to Scheme 9.



Scheme 9. The catalytic hydride polyaddition reaction of α,ω-dihydridepoly(dimethylsiloxanes) and 1,7-divinyl-1,7-dimethyl-3,5,9,11-tetraphenyltricyclohexasiloxane, where: R=Me, Ph; n=0 ÷ 86

New cyclolinear carbosiloxane copolymers containing organotricyclohexasiloxane fragments in backbones were synthesized in the reaction. They represent viscous liquids with a molecular mass varying in the range of $35\times10^3 - 45\times10^3$.

The influence of organotricyclohexasiloxane fragments in carbosiloxane copolymer on thermal oxidative degradation proceeding was studied. It is found that the increase in concentration of rigid organo-tricyclohexasiloxane fragments in linear chains of polymers increases their resistance to thermal oxidative degradation. For example, a 15 % mass loss of structure VII copolymers (R=Ph, *n*=74 and R=Me, *n*=86) is observed at 380 and 420 °C, respectively. For copolymer with *n*=0, it is observed at 540 °C.

Thus, the increase of cyclic fragments' concentration in the linear chain induces the rise of macromolecular chain rigidity and leads to the formation of a one-phase system. The increase of cyclic fragments' concentration in the macromolecular chain raises the thermal oxidative stability of copolymers.

4. Conclusions

It was observed that the rate and depth of polyaddition decrease with the increase in α, ω-dihydridedimethylsiloxanes chain length.

The synthesized carbosiloxane copolymers with disilylethylene groups in the main chain possess less thermal-oxidative stability in comparison with polyorganosiloxane analogs, but they have greater thermal stability in the absence of oxygen.

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Received: January 18, 2024 / Revised: February 29, 2024 / Accepted: April 11, 2024

ЦИКЛІЧНІ КРЕМНІЙОРГАНІЧНІ КОПОЛІМЕРИ: СИНТЕЗ ТА ДОСЛІДЖЕННЯ: ОГЛЯД

Анотація. *Розглянуто синтез і дослідження циклічних кремнійорганічних полімерів з моно- та поліциклічними фрагментами в бічному ланцюзі. Для одержання моноциклічних полімерів використано реакцію гідросилілювання 1-гідро-3-вінілгексаметилциклотетрасилоксану. Реакцію проводили в розчині* CCl_4 *при 75°C в присутності каталізатора Спаєра* ($H_2PtCl_6 \cdot 6H_2O$) *з отриманням полімеру, в'язкотекучого за кімнатної температури. Полімери досліджували методом ЯМР-спектроскопії. Полі(карбосилоксан) з циклічними фрагментами в метилсилоксановій основі синтезували через гідридне поліприєднання дивінілорганоциклосилоксану до дигідродиметилсилоксану. Напівкількісна оцінка, проведена за допомогою ЯМР-спектроскопії, показала, що співвідношення ізомерних 1,3- і 1,5-циклічних структур становить 1:1. Рентгеноструктурні дослідження показали, що кополімери є однофазними аморфними системами. Також в огляді обговорено синтез і дослідження кополімерів карбосилоксану, що містять гнучкі диметилсилоксанові та декаорганотрициклодекасилоксанові фрагменти в макроланцюзі. Гідридне поліприєднання дивінілвмісних сполук проведено для* α,ω*-дигідриддиметилсилоксанів різної довжини. Синтезовані кополімери охарактеризовано методами рентгенівської дифракції та ТГА.*

Ключові слова: *кремнійорганічні полімери, гідросилілювання, каталізатор Спаєра, карбосилоксанові кополімери.*