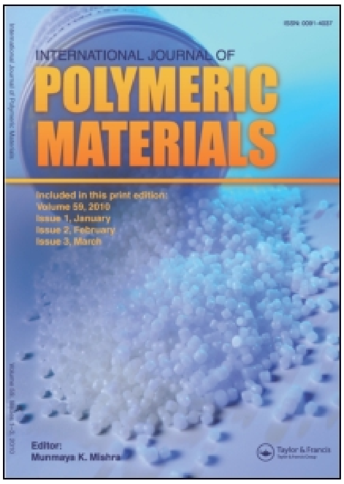


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Dehydrocondensation and hydrosilylation reactions of methylhydridesiloxane with allyl alcohol

O. Mukbaniani[a,b]; G. Gurgenidze[c]; L. Khananashvili[c]; S. Meladze[d]
[a] I. Javakhishvili Tbilisi State University, Tbilisi, Georgia [b] Branch of Tbilisi State University, Sukhumi State University, Tbilisi, Georgia [c] I. Javakhishvili Tbilisi State University, I. Tbilisi, Georgia [d] The Georgian Institute of Consumers' Association, Tbilisi, Georgia

To cite this Article Mukbaniani, O. , Gurgenidze, G. , Khananashvili, L. and Meladze, S.(2003) 'Dehydrocondensation and hydrosilylation reactions of methylhydridesiloxane with allyl alcohol', International Journal of Polymeric Materials, 52: 10, 861 — 876

To link to this Article: DOI: 10.1080/713743644

URL: http://dx.doi.org/10.1080/713743644

International Journal of Polymeric Materials, 52:861–876, 2003
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390225101

DEHYDROCONDENSATION AND HYDROSILYLATION REACTIONS OF METHYLHYDRIDESILOXANE WITH ALLYL ALCOHOL

O. Mukbaniani
I. Javakhishvili Tbilisi State University, I. Chavchavadze Ave., Tbilisi, Georgia, and Sukhumi State University, Branch of Tbilisi State University, Tbilisi, Georgia

G. Gurgenidze
L. Khananashvili
I. Javakhishvili Tbilisi State University, I. Tbilisi, Georgia

S. Meladze
The Georgian Institute of Consumers' Association, Tbilisi, Georgia

The reaction of dehydrocondensation of α,ω-bis(trimethylsiloxy)methylhydridesiloxane ($n \approx 53$) with allyl alcohol at various ratios of initial compounds, in the presence of anhydrous powders like caustic potassium and platinum chlorohydric acid has been investigated. It was established that in the presence of caustic potassium dehydrocondensation reaction takes place and methylsiloxane oligomers with allylic groups in side chain have been obtained. In the presence of platinum chlorohydric acid competetive dehydrocondensation and hydrosilylation reactions take place with formation of oligomers with various chain links. In late stages of the reaction three-dimensional systems were obtained. During dehydrocondensation the reaction order, reaction rate constants and activation energy were found. The structure of the synthesized oligomers were determined by IR and NMR spectra data. Gel permeation chromatography, differential scanning calorimetric and X-ray analysis of the synthesized oligomers were carried out.

Keywords: dehydrocondensation, hydrosilylation, methylhydridesiloxane

Received 7 April 2001, in final form 13 April 2001.

Address correspondence to O. Mukbaniani, I. Javakhishvili Tbilisi State University, I. Chavchavadze Avenue, 1, 380028 Tbilisi, Georgia. E-mail: omarimu@yahoo.com

INTRODUCTION

It is known that compounds with $\equiv$Si-H bonds react with water with elimination of hydrogen in the presence of alkali catalysts [1].

The reaction of catalytic dehydrocondensation between $\equiv$Si-H containing compounds and hydroxyl-containing organic compounds proceeds similarly with isolation of hydrogen [2, 3]. In the reactions of catalytic dehydrocondensation of hydrideorganosilanes with hydroxyl-containing organic compounds, catalysts are used such as colloid nickel, anhydrous zinc chloride, platinum chlorohydric acid [3, 4]. It was shown [5], that in the reaction of dehydrocondensation of dihydrideorganocyclosiloxanes with dihydroxyorganocyclosiloxanes platinum chlorohydric acid works as caustic potassium and activation energy has the same values. But on the other hand it is known that platinum chlorohydric acid is catalyst of hydrosilylation [6]. The reaction capacity of $\equiv$Si—H bond is determined by catalyst nature and amount, reaction temperature, reactant concentration, solvent character, etc. [7, 8]. By the authors [9] it was shown that during dehydrocondensation of hydride-containing organosiloxanes with hydroxyl-containing organosilanes and siloxanes in the presence of powder-like caustic potassium as a nucleophilic catalyst, the competing reaction of dialkylsiloxane elimination does not take place, which is explained by a high reaction rate of the dehydrocondensation process.

EXPERIMENTAL PART

The starting materials for the synthesis of comb-type methylsiloxanes with allyl and propanol groups in the side chain were α,ω-bis-(trimethylsiloxy)methylhydridesiloxane and allyl alcohol.

The initial α,ω-bis(trimethylsiloxy)methylhydridesiloxane with a degree of polymerization $n \approx 53$ was usefd as received from Nuncritz GMBS. The organic solvents were cleaned by drying and distillation.

IR spectra all of samples have been taken on an UR-20 instrument from KBr pellets, while the ^{1}H NMR spectra on a “Perkin-Elmer” at operating frequency of 250 MHz. All spectra were obtained with the use of $CDCl_3$ as solvent and internal standard. A Perkin-Elmer DSC-2 differential scanning calorimeter was used to determine TGA and the thermal transitions (Tg) were read at the maximum of the endothermic or exothermic peaks. Heating and cooling scanning rates were 10 deg/min.

Gel permeation chromatography investigation was carried out using a Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastyragel columns. Sample concentrations were approximately 3% by weight in toluene and typical injection volume for the siloxane was 5 μL standardization of the GPC was accomplished by the use of styrene or polydimethylsiloxane standards with known molecular weight.

Wide angle X-ray diffractograms were taken on a "DRON-2" instrument. A-Cu_α were measured without a filter, the angular velocity of the motor $\omega = 2$ deg/min.

Dehydrocondensation Reaction of *α,ω*-Bis(Trimethylsiloxy)Methylhydridesiloxane with Allyl Alcohol

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

The reagents were placed in the flask and thermostated in an oil bath until constant temperature was reached. Then the catalyst was introduced. After that hydrogen started releasing. Hydrogen was collected in the gasometer. After the reaction finished the solvent was removed (if caustic potassium was used as a catalyst, the reaction products were washed to neutral medium). The hydrosilylation reaction was carried out by the above reaction using platinum chlorohydric acid as a catalyst.

Hydride Addition of *α,ω*-Bis(Trimethylsiloxy)Methylhydridesiloxane to Allyl Alcohol

The hydrosilylation reaction was carried out in a three-necked flask equipped with stirrer, reflux condenser and calcium chloride drying tube. The initial reagents were placed in the flask and thermostated in an oil bath until constant temperature was achieved. 0,1 M solution of platinum chlorohydric acid in tetrahydrofuran ($5 \div 9 \times 10^{-5}$ g per 1,0 g of starting substance) was used as a catalyst. The reaction was carried out in an argon atmosphere in anhydrous toluene solution, at temperature range $30 \div 40\,^{\circ}C$. Then the reaction mixture was connected to the vacuum and the toluene and unreacted allyl alcohol were removed at $30 \div 40\,^{\circ}C$.

RESULTS AND DISCUSSION

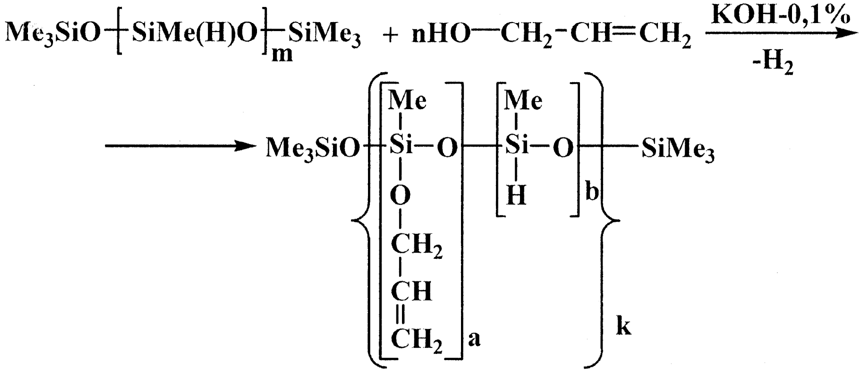
The main task of our work was the synthesis of comb-type silicon organic oligomers both with unsaturated groups and with hydroxyl groups in the side chain. As initial reagents α,ω-bis(trimethylsiloxy) methylhydridesiloxane and allyl-alcohol were used. For the purpose of synthesis of comb-type siliconorganic oligomers with oxiallyl fragments in the side chain, the reaction of dehydrocondensation at 1:53 and 1:26,5 mole ratio of initial components in the presence of 0,1% anhydrous powder-like caustic potassium has been carried out. Because the initial compounds are insoluble liquids, the reaction of dehydrocondensation was carried out in anhydrous toluene ($C \approx 0{,}0856$ mole/l), in the temperature range $20 \div 40\,^{\circ}C$.

Preliminary heating of the initial compounds for 4 h in the presence of KOH (0,1% of total mass of the initial components) or 0,1 M of platinum chlorohydric acid solution in tetrahydrofuran ($\sim 5 \div 9 \times 10^{-5}$ g per gram of reaction substances) in the temperature range $40 - 50\,^{\circ}C$ showed that polymerization of allyl-alcohol, or other changes due to break of siloxane backbone, or elimination of methane in methylhydridesiloxane do not take place. Besides, there are no changes in the NMR spectra of initial compounds.

The reaction of catalytic dehydrocondensation was examined at different temperatures (20, 30 and 40 °C) during which the generation of hydrogen was observed.

Figure 1 showed the dependence of the Si—H% concentration decreases on the time. As seen from Figure 1, with the temperature rise in the reaction of catalytic dehydrocondensation, the hydrogen generation increases from 90% (20 °C) up to 97% (40 °C). At 1:53 ratio of initial compounds, the reaction mainly proceeds during the first thirty minutes. As is seen from Figure 2 during dehydrocondensation in 1:26,5 mole ratio of initial compounds, the rate of dehydrocondensation increases up to 100%.

The reaction of dehydrocondensation proceeds according to the following scheme:



$$\mathrm{Me_3SiO{+}\left[SiMe(H)O\right]_m SiMe_3} + \mathrm{nHO{-}CH_2{-}CH{=}CH_2} \xrightarrow[\mathrm{-H_2}]{\mathrm{KOH\text{-}0,1\%}} \mathrm{Me_3SiO}\left\{\left[\begin{matrix}\mathrm{Me}\\ | \\ \mathrm{Si{-}O}\\ | \\ \mathrm{O}\\ | \\ \mathrm{CH_2}\\ | \\ \mathrm{CH}\\ \| \\ \mathrm{CH_2}\end{matrix}\right]_a \left[\begin{matrix}\mathrm{Me}\\ | \\ \mathrm{Si{-}O}\\ | \\ \mathrm{H}\end{matrix}\right]_b\right\}_k \mathrm{SiMe_3}$$

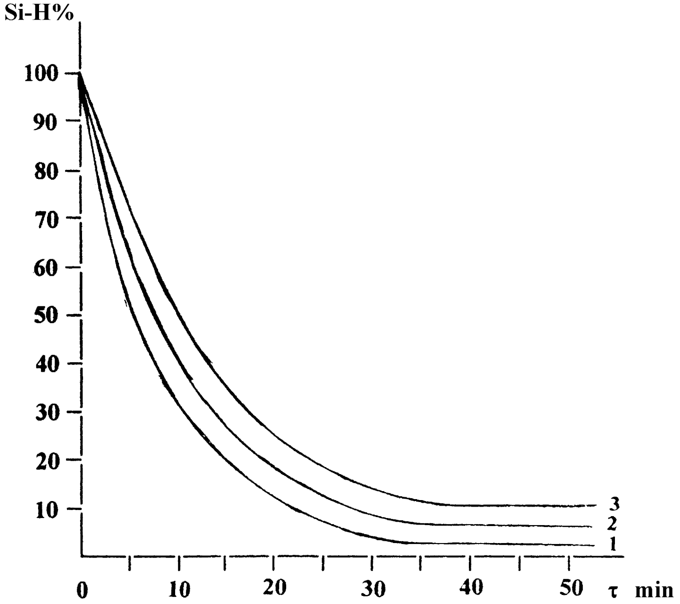


FIGURE 1 Dependence of changes of active Si-H% groups on time upon hydride addition of α,ω-bis(trimethylsiloxy)methylhydridesiloxane to allyl-alcohol, where curve 1 is at 40 °C, curve 2 is at 30 °C and curve 3 is at 20 °C (ratio 1:53).

The obtained products were transparent colorless oils soluble in ordinary organic solvents with $\eta_{sp} \approx 0{,}09 \div 0{,}13$. It was established that in the beginning stages the reaction of dehydrocondensation is a second order reaction. In Figures 3 and 4 a direct dependence of the reverse concentration of the reactants on the time is shown. From which the reaction rate constants at various temperatures and at various ratios of initial compounds were calculated. The reaction rate constants at 1:53 ratio is $K_{40^\circ C} \approx 2{,}4751$; $K_{30^\circ C} \approx 1{,}7322$; $K_{20^\circ C} \approx 1{,}1917$ and temperatural coeficient of this reaction is about $\gamma \approx 1{,}45$ and the reaction rate constants at 1:26,5 ratio is $K_{40^\circ C} \approx 1{,}4825$; $K_{30^\circ C} \approx 1{,}0355$; $K_{20^\circ C} \approx 0{,}7265$ and the temperatural coefficient of this reaction is $\gamma \approx 1{,}42$.

Figures 5 and 6 show the dependence of the reaction rate constants logarithm on inverse temperature, from which the activation energies of the reaction of dehydrocondensation were calculated. For the 1:53 ratio the activation energy is equal to $E \approx 29{,}2$ KJ/mole.

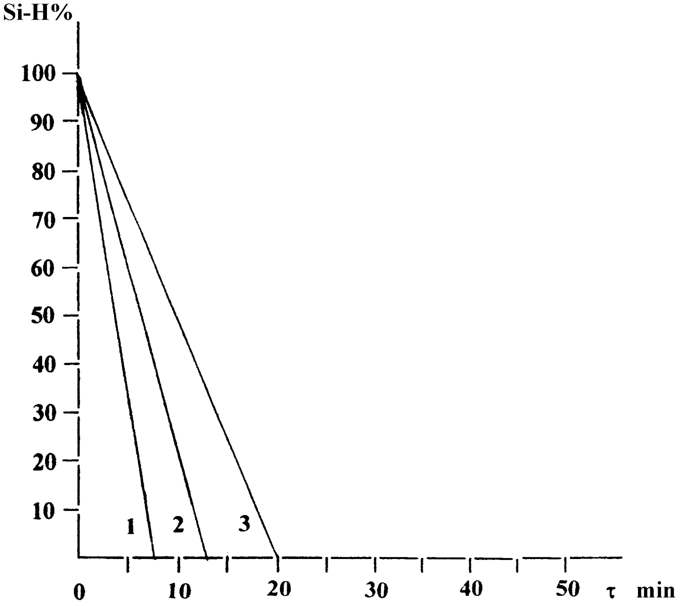


FIGURE 2 Dependence of changes of active Si-H% groups on time upon hydride addition of α,ω-bis(trimethylsiloxy)methylhydridesiloxane to allyl-alcohol, where curve 1 is at 40°C, curve 2 is at 30°C and curve 3 is at 20°C (ratio 1:26,5).

This value of activation energy is near the activation energy of the reaction of dehydrocondensation of hydroxy(alkyl)thioethanes to methylhydridesiloxane, which is $E \approx 31,6$ KJ/mole [10]. For the 1;26,5 ratio the activation energy is $E \approx 28,5$ KJ/mole. In the IR spectra of the synthesized oligomers one can observe absorbtion bands characteristic of asymmetric valence oscilation of Si-O-Si and Si-O-C bonds in region 1020 and 1080 cm^{-1}. In the region 1275 and 2160 cm^{-1}, one can observe absorption bands characteristic for Si-Me and unreacted Si-H bonds respectively. In ^1H NMR spectrum of oligomer III, Figure 7 one can observe singlet signals of methyl protons with chemical shift $\delta \approx 0,1$ ppm, methylene protons in CH_2O group with chemical shift $\delta \approx 4,12$ ppm, complicated multiplet for methylene protons in $CH_2=$ group with chemical shift in the range $\delta \approx 4,9 \div 5$, ppm, complicated multiplet for CH= group with chemical shift $\delta \approx 5,7 \div 5,9$ ppm, with centre at $\delta \approx 5,8$ ppm. Figure 8 showed ^{13}C NMR spectrum of oligomer III. In the spectrum one can observe signal for carbon atom in the

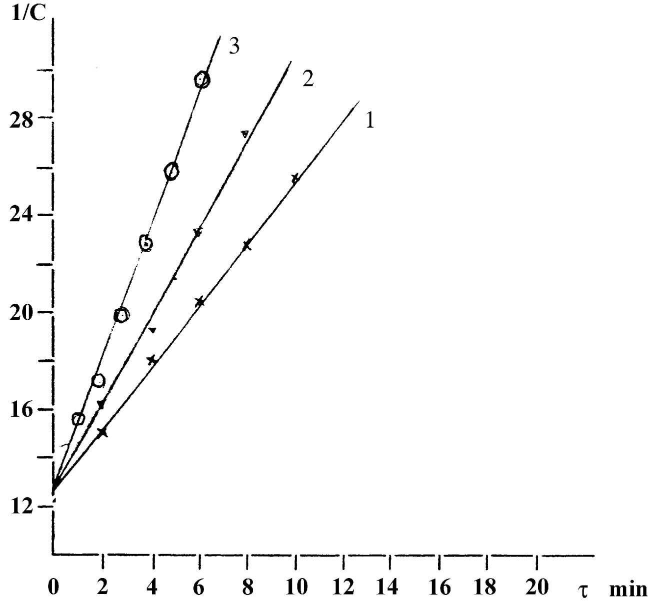


FIGURE 3 Dependence of inverse concentration on the time, where curve 1 is at 20 °C, curve 2 at 30 °C and curve 3 is at 40 °C (ratio 1:53).

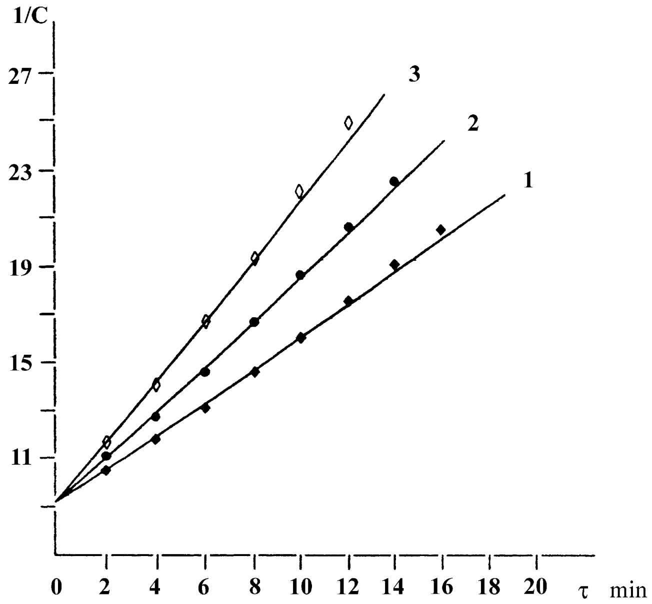


FIGURE 4 Dependence of inverse concentration on the time, where curve 1 is at 20 °C, curve 2 at 30 °C and curve 3 is at 40 °C (ratio 1:26,5).

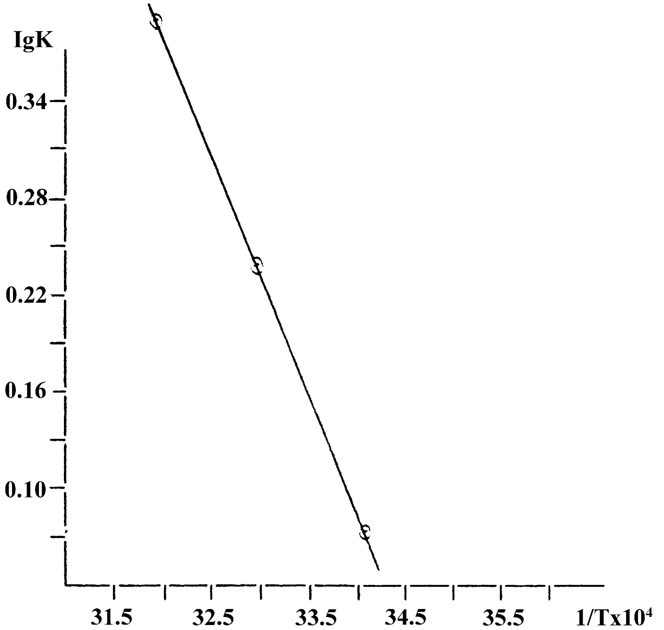


FIGURE 5 Dependence of inverse temperature on the rate constants logarithm of upon hydride addition of α,ω-bis(trimethylsiloxy)methylhydridesiloxane to allyl-alcohol (ratio 1:53).

CH_2= fragment with chemical shift $\delta \approx 134{,}94$ ppm, for the carbon in the CH= fragment $\delta \approx 113{,}06$ ppm and in the CH_2O fragment $\delta \approx 61{,}79$ ppm.

For the purpose of synthesis of methylsiloxane oligomers with hydroxy groups in the side chain the reaction of hydrosilylation of α,ω-bis(trimethylsiloxy)methylhydridesiloxane to allyl-alcohol has been carried out in the ratio of initial components 1:53, in the presence of 0,1 M solution of platinum chlorohydric acid in tetrahydrofuran in the temperature range 30–40°C. Hydrosilylation reaction was investigated both in melt condition and in solution. During the reaction in melt condition the reaction proceeds very energetically and gelation rapidly takes place. As is known from the literature [11] platinum chlorohydric acid is a catalyst of hydrosilylation as well as the catalyst of dehydrocondensation. So, during this reaction competitive reactions may proceed according to the following scheme:

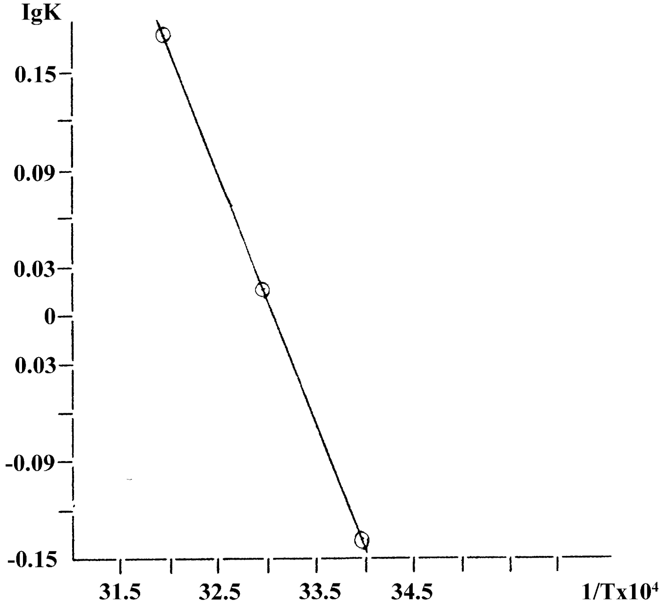


FIGURE 6 Dependence of inverse temperature on the rate constants logarithm of upon hydride addition of α,ω-bis(trimethylsiloxy)methylhydridesiloxane to allyl-alcohol (ratio 1:26,5).

$$\equiv Si{-}H + CH_2{=}CH{-}CH_2OH \xrightarrow{H_2PtCl_6} \equiv Si{-}CH_2{-}CH_2{-}CH_2OH$$
$$\equiv Si{-}H + HO{-}CH_2{-}CH{=}CH_2 \xrightarrow[-H_2]{H_2PtCl_6} \equiv Si{-}O{-}CH_2{-}CH{=}CH_2$$

In the investigation it was established that in the presence of platinum chlorohydric acid during the hydrosilylation reaction, the dehydrocondensation reaction also takes place. To minimize crosslinking and to receive soluble oligomers the above mentioned reactions were carried out in dilute 40% solution of anhydrous toluene. In spite of that the reaction was carried out in dilute toluene solution at late stages of the reaction crosslinking took place. It must be noted that during the hydrosilylation reaction the release of hydrogen was observed. It was determined that during this reaction hydrosilylation proceeds about ~20%, and catalytic dehydrocondensation proceeds about ~50%, after that the crosslinking began.

So, the above mentioned hydrosilylation-dehydrocondensation reactions at the first stages proceeds with formation of various oligomers, according to the following scheme:

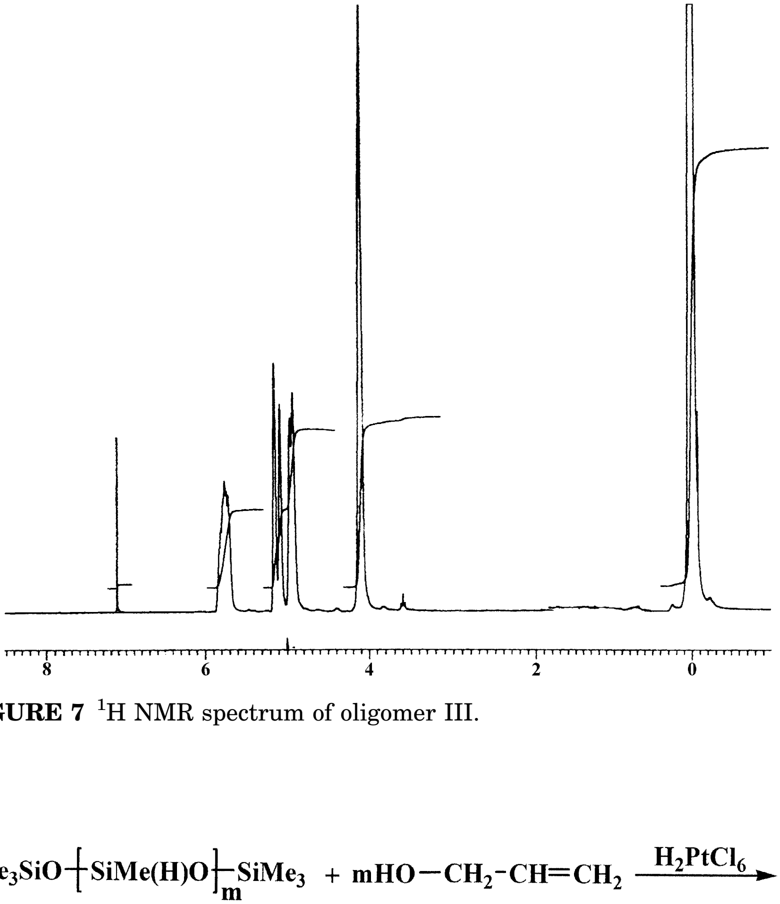
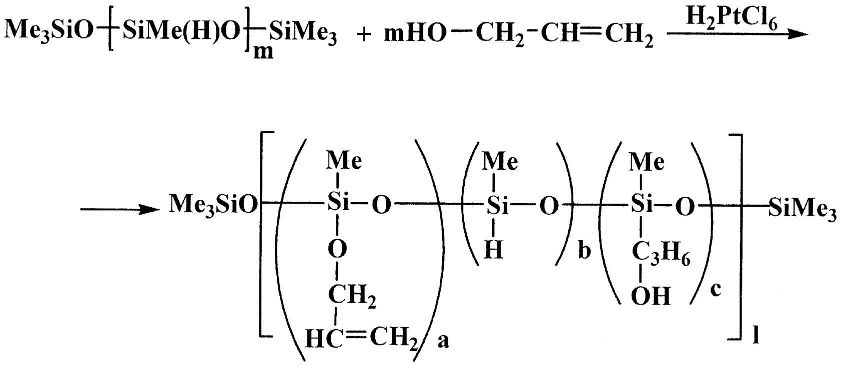


FIGURE 7 ^{1}H NMR spectrum of oligomer III.



$$Me_3SiO\left[SiMe(H)O\right]_m SiMe_3 + mHO-CH_2-CH=CH_2 \xrightarrow{H_2PtCl_6}$$

$$\longrightarrow Me_3SiO\left[\left(\begin{array}{c}Me\\|\\-Si-O-\\|\\O\\|\\CH_2\\|\\HC=CH_2\end{array}\right)_a \left(\begin{array}{c}Me\\|\\-Si-O-\\|\\H\end{array}\right)_b \left(\begin{array}{c}Me\\|\\-Si-O-\\|\\C_3H_6\\|\\OH\end{array}\right)_c\right]_l SiMe_3$$

Where: $m \approx 53$, $(a+b+c)l = m$ – VII.

After this the crosslinking processes take place. The formation of three-dimensional systems may proceed with competitive reactions:

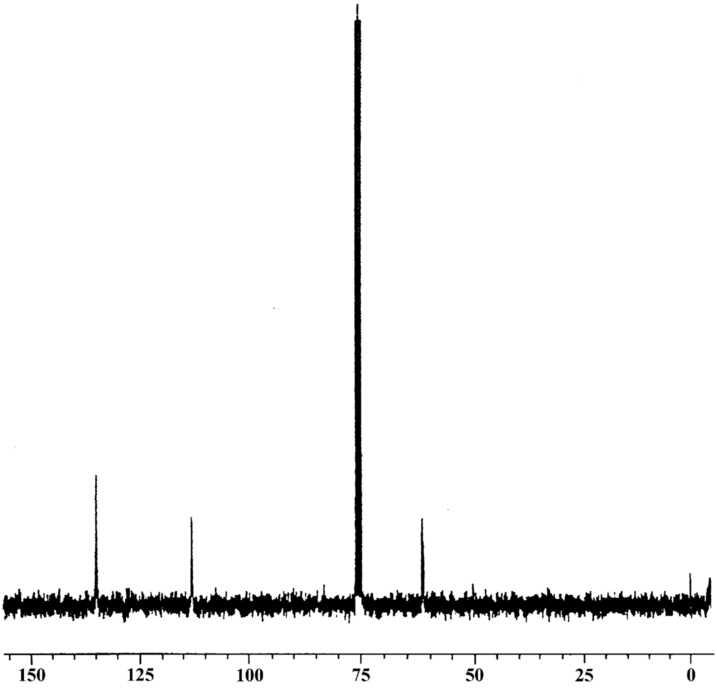


FIGURE 8 ^{13}C NMR spectrum of oligomer III.

$$\equiv Si-C_3H_6-OH+H-Si\equiv \xrightarrow[-H_2]{H_2PtCl_6} \equiv Si-C_3H_6\text{-}O-Si\equiv$$

$$\equiv Si-O\text{-}CH_2\text{-}CH=CH_2+H-Si\equiv \xrightarrow{H_2PtCl_6} \equiv Si-O\text{-}C_3H_6\text{-}Si\equiv$$

From the crosslinked three-dimensional systems the soluble part was taken, on which ^1H NMR investigation was carried out. From Figure 9 it is seen that the hydride addition follows Farmer rule as well as Markovnikov rule with the ratio 3:1. In the NMR spectra of soluble part of oligomer VII one can observe the singlet signal characteristic for methyl protons at silicon atoms with chemical shift $\delta \approx 0,1$ ppm, for methyl protons in $CH_3-CH=$ fragment and for CH protons with chemical shifts $\delta \approx 0,8$ and $\delta \approx 1,7$ ppm, these fragments may be obtained during Markovnikov addition, for CH_2 protons in $-CH_2O-$ and $\equiv Si-CH_2-$ fragment (Markovnikov rule) with chemical shifts $\delta \approx 1,7$ and $\delta \approx 3,7$ ppm accordingly. During the reaction of Farmer rule in the NMR spectra one can observe singlet signals with chemical shifts $\delta \approx 1,2$; $\delta \approx 1,5$ and $\delta \approx 3,8$ ppm characteristic for

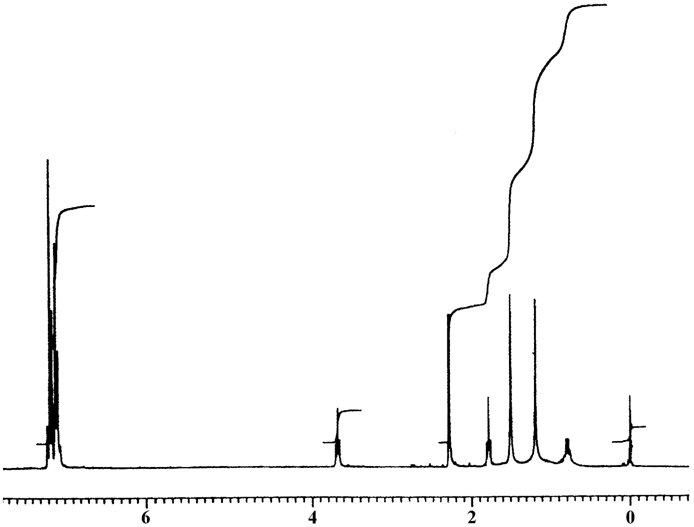
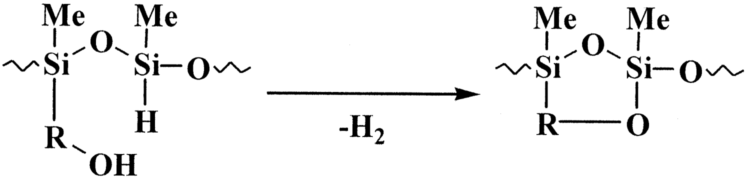
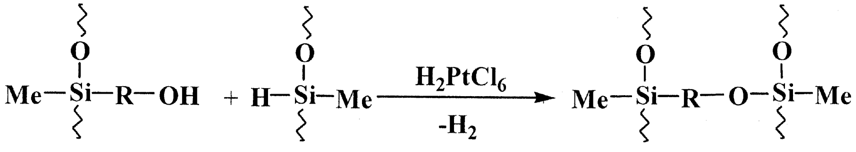


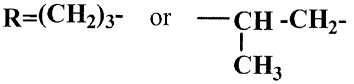
FIGURE 9 ^1H NMR spectrum of oligomer VII.

protons in $\equiv Si-CH_2-, -CH_2-$ and CH_2O and CH_2O protons respectively. In the spectra the resonance signals for hydroxyl groups is not observed, from which it is evident that in synthesized oligomers intra- and intermolecular reactions of dehydrocondensations, take place according to the following scheme:



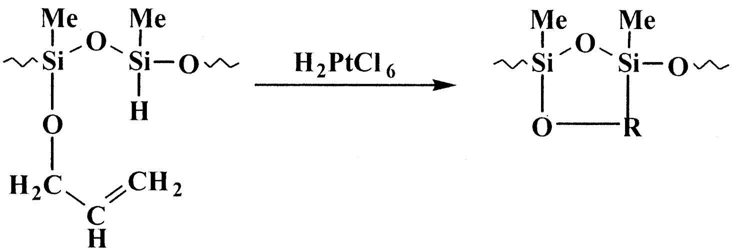
Intramolecular dehydrocondensation-cyclyzation



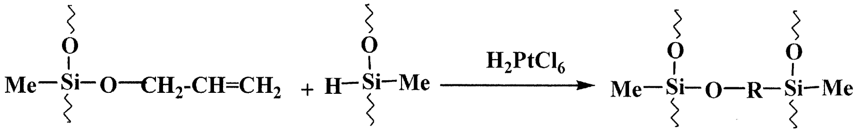

$R=(CH_2)_3-$ or $-\underset{\displaystyle CH_3}{CH}-CH_2-$

Intermolecular dehydrocondensation.

Alternatively, if the reaction proceeds by dehydrocondensation path, in the synthesized oligomers resonance signals for unsaturated allyl fragments in the range 5,0 ÷ 6,0 ppm must be observed. But in the spectrum Figure 9 there are no such resonance signals, which show that the fragment $\equiv Si-O-CH_2-CH=CH_2$ may enter the intra- and intermolecular hydride additions by the schemes:



Intramolecular hydride addition



Intermolecular hydride addition, where: $R = -(CH_2)_3-$, or $-CH(CH_3)-CH_2-$.

Gel permeation chromatographic analysis of oligomers was carried out. In Figure 10 the molecular weight and molecular weight distribution of oligomer III are presented. Average molecular mass of oligomers changes in range $\bar{M}_W \approx 4,8 \times 10^3 \div 6,5 \times 10^3$ and polydispersity $D = 2,5 \div 4,7$. By differential scanning calorimetric investigation it was shown, that oligomers I, III and VI are characterized by one glass transition temperature (T_g). The value of this T_g are in the temperature range $-123 \div -110\,^{\circ}C$ (see Table 1). The oligomers are characterized with low thermal-oxidative stability. The 5% mass loss is observed in the temperature range 230–250 °C. The main destruction process proceeds in the temperature range 270–540 °C. After 550 °C mass losses do not occur.

Wide angle X-ray analysis of synthesized oligomers was carried out. As is seen from Figure 11, the oligomers with allylic groups in the side chain are one phase amorphous systems and the maximum

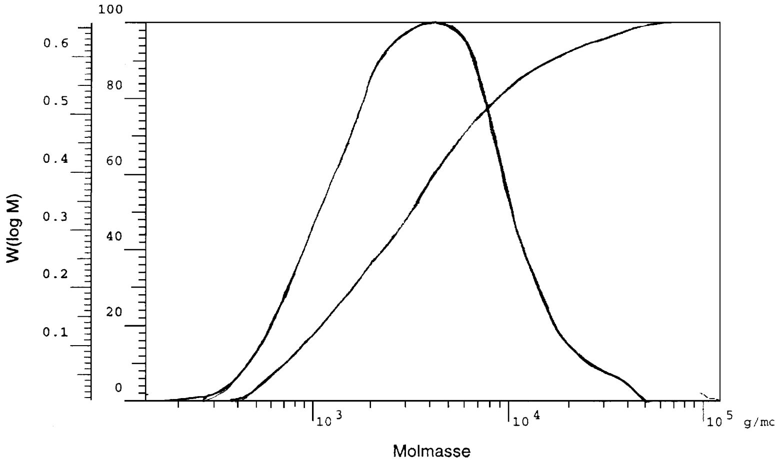


FIGURE 10 Gel permeation chromatographic curves of oligomer III.

values of interchain distance of oligomers change in the range $d_1 \approx 9{,}30 \div 9{,}40$ Å.

So, by catalytic dehydrocondensation of α,ω-bis(trimethylsiloxy) methylhydridesiloxane with allyl alcohol, methylhydridesiloxanes with oxyallyl side chain groups were synthesized by us for the first time. Soluble methyl-hydridesiloxane with oxiallyl and propanol groups in the side chain were obtained by hydride addition of α,ω-bis(trimethylsiloxy)methylhydridesiloxane with allyl alcohol in the presence of platinum chlorohydric acid in a low stage of conversion

TABLE 1 Some Physical-Chemical Properties Methylhydridesiloxanes with Organic Side Groups

$\partial\omega$	η_{sp}*	d1, Å	T_g, °C	$\bar{M}_w$	5% mass losses	Residual mass, %	Yield, %
I	0,04		– 116	6030			90
II	0,04		– 116				94
III	0,05	9,30	– 110	6500	250	21	98
IV	0,03						100
V	0,04	9,12	– 123				100
VI	0,04			4800	230	17	100
VII	0,05	9,23	– 110		240	23	32

*In 1% toluene solution at 25 °C.

Average molecular weights were determined by gel permeation chromatographic method.

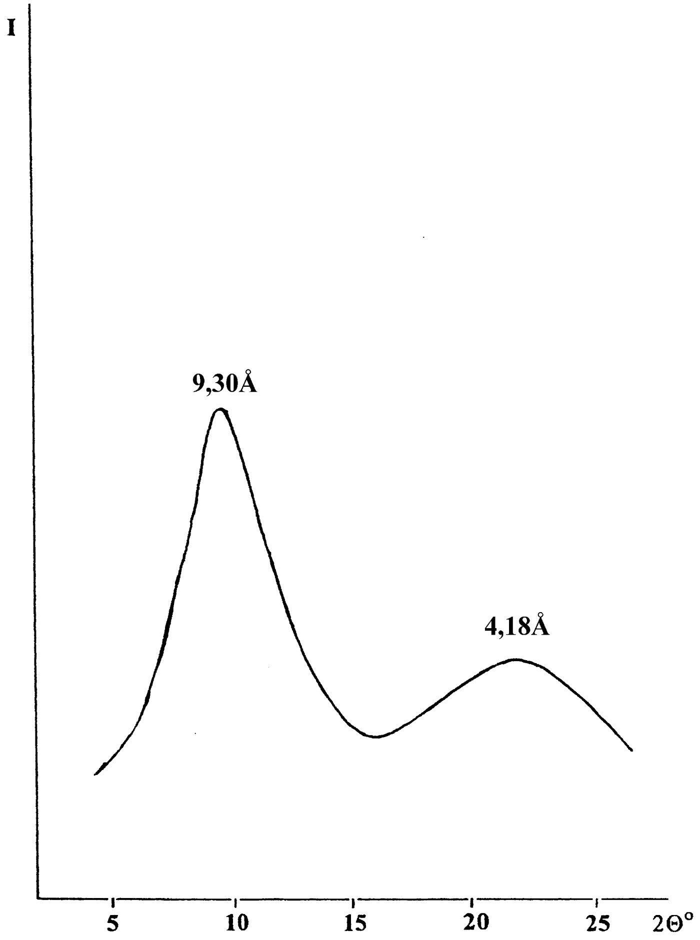


FIGURE 11 X-ray pattern of oligomer III.

of active Si –H groups ($\sim$77%). The synthesized comb-type methylhydridesiloxane with oxyallyl and propanol side groups are interesting products for modification of carbochain elastomers and as new thermosetting polymers.

REFERENCES

[1] Price, P. P. (1947). *J. AmChem. Soc.*, **69**, 2600.
[2] Dolgov, B. N. (1958). Chemistry and Practical Application of Organosilicon Compounds; *Chemical Library of Technical Information*, Leningrad, **1**, 18 (in Russian).

[3] Andrianov, K. A. and Zavin, B. G. (1960). *Zhurn. Neorg. Khim.*, **12**, 2216.

[4] Borisov, S. N., Sviridova, I. G. and Orlova, V. S. (1966). *Zhurn. Obshch. Khim.*, **36**, 687; (1966). *Chem. Abstr.*, **65**, 8946b.

[5] Mukbaniani, O., Khananashvili, L., Koiava, N. A., Porchkhidze, G. and Yu. Tolchinski (1992). *Inten. J. Polym. Mater.*, **17**, 113.

[6] Khananashvili, L. M., Mukbaniani, O. V., Inaridze, I. A., Porchkhidze, G. V. and Koberidze, Kh. E. (1998). *Eur. Polym. J.*, **34**, 43/4, 581.

[7] Dolgov, B. N., Kharitonov, I. P. and Voronkov, M. G. (1954). *Zhurn. Obshch. Khim.*, **24**, 861; (1955). *Chem. Abstr.*, **49**, 8094i.

[8] Beines, J. and Eaborn, C. (1955). *J. Chem. Soc.*, p. 4023.

[9] Lee, C. L. (1966). *J. Organomet. Chem.*, **6**, 603.

[10] Chachua, E., Mukbaniani, O., Gadzhiev-Shengelia, D., Karchkhadze, M. and Khananashvili, L. (1998). *Bull. of the Georgian Academy of Sci.*, **43**, 58.