

Synthesis of Thermoreactive Polysiloxanes with Cyclic Fragments in the Side Chain

Omari Mukbaniani, Tamara Tatrishvili, Giorgi Titvinidze, Sopho Patsatsia

Department of Macromolecular Chemistry, Iv. Javakishvili Tbilisi State University, I, Chavchavadze Avenue, 1, 0128, Tbilisi, Georgia

Received 24 September 2008; accepted 4 April 2009

DOI 10.1002/app.30530

Published online 15 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The synthesis of polysiloxanes with pendant unsaturated cyclic fragments have been successfully performed by hydrosilylation reactions of polymethylhydrosiloxane with 4-vinyl-1-cyclohexene in the presence of platinum hydrochloric acid (0.1 M solution in THF), Karstedt's catalyst ($\text{Pt}_2[(\text{VinSiMe}_2)_2\text{O}]_3$) and platinum on the charcoal (5%). Reactions were carried out at various temperatures with different ratios of initial compounds. It was shown, that not all active $\equiv\text{Si-H}$ groups take part in the hydrosilylation reaction. Some kinetic parameters of reactions were studied. The synthesized oligomers were characterized by FTIR, ^1H , ^{13}C , H,H-COSY, and C,H-corre-

lation NMR spectroscopy. Calculations using the quantum-chemical semi empirical AM1 method for modeling reactions between methylmethoxysilane $[\text{Me}(\text{MeO})_2\text{SiH}]$ and 4-vinyl-1-cyclohexene were performed to evaluate possible reaction paths. Synthesized oligomers were characterized by gel-permeation chromatography, differential scanning calorimetric, thermogravimetric, and wide-angle X-ray analyses. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 892–900, 2009

Key words: hydrosilylation; methylhydrosiloxane oligomers; cross-linking; kinetics

INTRODUCTION

Polysiloxanes are of particular interest due to their extremely low glass transition temperatures and flexibility, their hydrophobic surface properties, good thermal stability, and excellent flame retardant.^{1–4}

In the past years, catalytic grafting of polymethylhydrosiloxane (PMHS) has emerged as an alternative route for the synthesis of new silicon-organic polymers owing different properties. Low cost, easy availability, and the presence of catalytically transformable $\equiv\text{Si-H}$ bonds in PMHS make it very attractive and interesting for macromolecular grafting.^{5,6} Organic functionalization of the polymer chain can lead to obtaining of a new polymers and oligomers owing various physical and chemical properties. For example, appropriate substitution on the polysiloxanes backbone can lead to various materials such as cross-linking agents,^{7,8} liquid crystals,^{9,10} fluorescent and electro luminiscent polymers,^{11,12} and non-linear optical materials.¹³

There are some information's about hydride addition reaction of ethyldichlorosilane to 4-vinyl-1-cyclohexene in the presence of Pt/C at 180°C temperature.

During this reaction hydrosilylation proceeds on the vinyl group and the yield of obtained 2-(4-cyclohexenyl)ethyldichlorosilane is about 81%¹⁴ and the reaction proceeds according to Scheme 1.

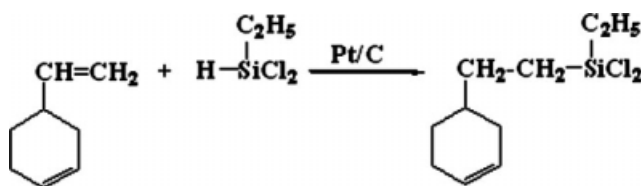
Although using H_2PtCl_6 as a catalyst the reaction proceeds at 100°C during 3 h with formation of monosilyl derivatives.^{15,16} It was shown that the same monosilyl derivative enter in hydrosilylation reaction with hydroorganochlorosilane in the presence of platinum catalyst with obtaining of disilyl derivatives in a high yield.¹⁷

Hydrosilylation reaction of 4-vinyl-1-cyclohexene with triorganohydrosilanes in the presence of ternary chelate catalysts, such as Ni, Mo, V, triphenylphosphine, and triethylaluminum¹⁸ proceeds with the vinyl group with formation of monosilyl derivatives. It was shown that the yield of obtained adduct depends on the structure of chelate catalysts and on the nature of used metals.

Hydrosilylation is a general term used, for the addition reaction of organic and inorganic silicon hydrides to molecules and macromolecules containing multiple bonds. The universal character of the process is reflected in the wide spectrum of usable unsaturated moieties.¹⁹ Hydrosilylation is most widely used reaction for grafting of PMHS. Chemical functionalization of polysiloxane chains involves preliminary introduction of side chains with functional groups. Introduced functional groups in side chains have ability to undergo further

Correspondence to: O. Mukbaniani (mukbaniani@tsu.ge).

Contract grant sponsor: Georgian National Science Foundation; contract grant number: GNSF/ST06/4-070.



Scheme 1 Hydride addition reaction of ethyldichlorosilane to 4-vinyl-1-cyclohexene.

modifications. The majority of functionalized siloxanes were designed to undergo thermally induced cross-linking, and to cure by hydrolytic processes or photochemically induced polymerization.^{4,20}

A number of articles currently deal with mechanistic aspects and directions of hydrosilylation processes and also with the search for new, improved, or less expensive convenient catalysts.

In this work, grafting of PMHS via hydrosilylation reactions with 4-vinyl-1-cyclohexene were investigated in the presence of several platinum catalysts. The rates and depths of reactions were evaluated in all cases. The thermoreactive methylsiloxane oligomers with unsaturated side fragments are interesting products for modification of carbochain elastomers and for obtaining of new siliconorganic rubbers.

EXPERIMENTAL PART

Materials

PMHSi (Aldrich), platinum hydrochloric acid (Aldrich), Karstedt's catalyst ($\text{Pt}_2[(\text{VinSiMe}_2)_2\text{O}]_3$)—platinum(0)—1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (solution in PDMS), platinum on the charcoal and 4-vinyl-1-cyclohexene (Aldrich) were used as received. Toluene and THF was dried over and distilled from sodium under an atmosphere of dry nitrogen. 0.1 M solution of platinum hydrochloric acid in THF was prepared and kept under nitrogen at low temperature.

Characterization

FTIR spectra were obtained on a Nicolet Nexus 470 machine with MCTB detector. ^1H , H,H COSY, ^{13}C NMR, and H,C-correlation NMR spectra were recorded on a 500 MHz Bruker NMR spectrometer, using CDCl_3 as the solvent and an internal standard. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 machine at the heating rate of 10 K/min. Differential scanning calorimetric investigation (DSC) was performed on a Perkin Elmer DSC-7 apparatus. Thermal transitions including glass transition temperatures T_g were taken as the maxima of the peaks. The heating and cooling scanning rates were 10 K min^{-1} .

Gel-permeation chromatographic investigation was carried out with the use of Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastaygel columns. Sample concentration was approximately 3% by weight in toluene and typical injection volume for the siloxane was 5 μL flow rate—1.0 ml/min standardization of the GPC was accomplished by the use of styrene or polydimethylsiloxane standards with the known molecular weight. Wide-angle X-ray diffractograms were taken on a DRON-2 (Burevestnik, Saint Petersburg, Russia) instrument. $A\text{-CuK}_\alpha$ was measured without a filter; the angular velocity of the motor was $\omega \approx 2 \text{ deg}\cdot\text{min}^{-1}$.

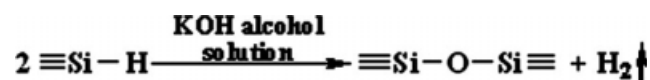
Determination of $\equiv\text{Si-H}$ content

The content of active $\equiv\text{Si-H}$ groups in oligomers was calculated on the basis of the following reaction (Scheme 2).

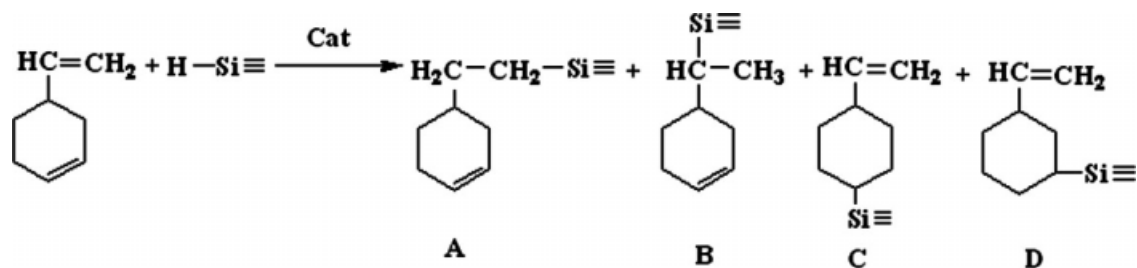
We place in a two-necked flask an exactly weighed amount of $\equiv\text{Si-H}$ containing oligomer, which should correspond to evolution of certain volume of hydrogen gas. We fit pressure-equalized dropping funnel with 0.5 M KOH alcohol solution onto the flask. We connect the flask with a gas burette, which we connect with a levelling bottle at the bottom part, by means of a silicon tube. We allow the system to stand for 10 min. The water level in the levelling bottle adjusts to the same level as that in the gas burette (V_1 , mL) is recorded. After, we add the 0.5 M KOH alcohol solution slowly. As hydrogen gas evolves, the water level goes downward. Thus, we need to keep the both water levels the same as each other so that we could equalize the pressure in the system to atmosphere. After the evolution of hydrogen gas completes (around 3–5 min), we record another 5 min later the value of the water level in the burette (V_2 , mL). The difference between V_2 and V_1 gives the volume of eliminated hydrogen gas (V , mL). The $\equiv\text{Si-H}$ content of an oligomer is given by the following:

$$\equiv\text{Si-H content} = 1000 PV/WRT(\text{mol}/100 \text{ g})$$

where P —atmospheric pressure at measurement (atm), V —gas volume captured (mL), W —sample weight (g), $R = 0.0082$ (gas constant) ($\text{l} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and T —temperature (K at measurement).²¹



Scheme 2 Reaction scheme of potassium hydroxide with hydrosilanes.



Scheme 3 Possible hydrosilylation reactions of hydrosilane with 4-vinyl-1-cyclohexene.

Synthesis

Catalytic hydrosilylation reaction of PMHS with 4-vinyl-1-cyclohexene in the presence of H_2PtCl_6

PMHS (0.9850 g, 0.43 mmol), 4-vinyl-1-cyclohexene (1.6595 g, 0.0153 mol) and 5.5 mL dry toluene were placed into the three-necked flask equipped with a magnetic stirrer, reflux condenser, and thermocouple in inert atmosphere. Then, the catalyst 0.1 M solution of platinum hydrochloric acid in tetrahydrofuran (7×10^{-5} g per 1.0 g of PMHS) was introduced. After the reaction completion, the solvent was partially eliminated, the reaction product was precipitated from toluene solution by *n*-hexane, and 2.4593 g (93 %) oligomer was obtained. The hydrosilylation reactions in the presence of other catalysts were carried out according to the above-mentioned method.

RESULTS AND DISCUSSION

For synthesis of methylsiloxane oligomers with unsaturated cyclic fragments in the side chain, we carried out hydrosilylation reactions of 4-vinyl-1-cyclohexene with PMHS in the presence of platinum hydrochloric acid (0.1 M in THF), Karstedt's catalyst ($\text{Pt}_2[(\text{VinSiMe}_2)_2\text{O}]_3$) and platinum on the charcoal. Hydrosilylation reactions were carried out with various molar ratios of initial compounds (1:35, 1 : 70 and 1 : 105). From the literature¹⁷ it is known that not all active

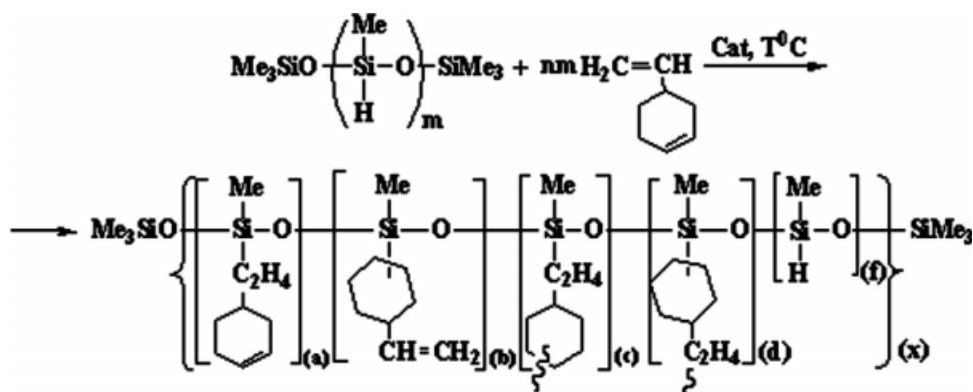
$\equiv\text{Si}-\text{H}$ groups participate in hydrosilylation reactions in case of stoichiometric ratio with respect to $\equiv\text{Si}-\text{H}$ bonds. We have taken 4-vinyl-1-cyclohexene in excess to achieve full hydrosilylation of PMHS.

Preliminary heating of initial compounds in the temperature range of 40–100°C in the presence of catalysts showed that in these conditions there is no polymerization of 4-vinyl-1-cyclohexene, nor destruction of siloxane backbones, nor elimination of methane from methylhydrosiloxane occurred. No changes in the NMR and FTIR spectra of initial compounds were found.

Without solvent, the reaction proceeds vigorously (especially in case of platinum hydrochloric acid and Karstedt's catalyst) and at initial stages of $\equiv\text{Si}-\text{H}$ bonds conversion ($\sim 30\%$) gelation takes place. To prevent gelation and investigate kinetic parameters, reaction were carried out in the toluene solution.

As it is seen from the structure of 4-vinyl-1-cyclohexene, it has two active centres for hydride addition of hydrosilane. Thus, hydrosilylation reaction of 4-vinyl-1-cyclohexene with PMHS may proceed in four different directions: anti-Markovnikov (A) and Markovnikov (B) addition to vinyl group and hydrosilylation to unsaturated bond in the cyclic fragment in the para (C) or meta (D) position (Scheme 3).

In general, we can represent hydrosilylation of α,ω -bis(trimethylsiloxy)methylhydrosiloxane with 4-vinyl-1-cyclohexene by the following Scheme 4.



Scheme 4 Hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydrosiloxane with 4-vinyl-1-cyclohexene.

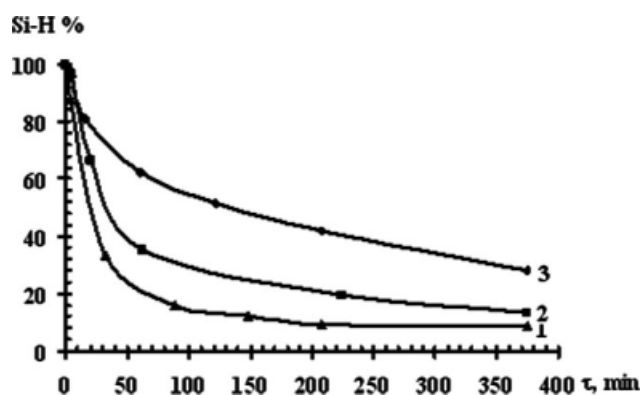


Figure 1 Dependence of changes of concentration of active $\equiv\text{Si-H}$ groups on the time, during hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydrosiloxane with 4-vinyl-1-cyclohexene, where curve 1 represents the values obtained at 60°C, curve 2 represents the values obtained at 50°C and curve 3 represents the values obtained at 40°C (H_2PtCl_6 , ratio 1 : 70).

Where $[(a)+(b)+(c)+(d)+(f)](x) = m \approx 35$; Cat— $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ - 40°C (I¹), 50°C (I²) and 60°C (I) (ratio 1 : 35). 40°C (II¹), 50°C (II²), 60°C (II) (ratio 1 : 70). 60°C (III) (ratio 1 : 105). 80°C (IV) (ratio 1 : 140). Cat—Pt/C - 80°C (V¹), 90°C (V²), 100°C (V) (ratio 1 : 70). Karstedt's catalyst, 70°C (VI¹), 80°C (VI²), 90°C (VI) (ratio 1 : 70).

As one can see from Figure 1 hydrosilylation reaction proceeds rapidly during the first hour and then slows down. The synthesized oligomers are vitreous liquid products, which are well soluble in aromatic type organic solvents with the specific viscosity $\eta_{\text{sp}} \approx 0.09 - 0.1$. Structures and composition of the oligomers were established by elemental and func-

tional analysis, FTIR spectra, ^1H , ^{13}C , $\text{H}_2\text{H-COSY}$, and C,H -correlation NMR spectral data. Some physical-chemical properties of the synthesized oligomers are presented in Table I.

We have studied some kinetic parameters for hydrosilylation reactions of PMHS with 4-vinyl-1-cyclohexene in the presence of H_2PtCl_6 with 1 : 70 ratios of initial compounds (1 : 2 stoichiometric ratio with respect to $\equiv\text{Si-H}$ bonds). From Figure 1, one can observe dependence of changes of active $\equiv\text{Si-H}$ groups on time. From Figure 1, it is evident that at 40°C hydrosilylation reaction proceeds with $\sim 75\%$ conversion of active $\equiv\text{Si-H}$ groups, whereas at 60°C hydrosilylation reaction proceeds with $\sim 91\%$ conversion. Consequently, with the rise of temperature, the conversion of active $\equiv\text{Si-H}$ groups increases.

Figure 2 shows dependence of reverse concentration on the time during the hydrosilylation reaction of PMHS with 4-vinyl-1-cyclohexene. One can see that at the initial stages, the hydrosilylation reaction is of second order. From the literature,²²⁻²⁴ it is known that hydrosilylation reactions as usual at initial stages are of a second order in case of stoichiometric ratio between initial compounds with respect to $\equiv\text{Si-H}$ bonds. According to experimental results increasing of concentrations of one of the initial compound does not change reaction order. The reaction rate constants of hydrosilylation reactions of PMHS with 4-vinyl-1-cyclohexene at various temperatures were determined, the values are listed below: $k_{60^\circ\text{C}} \approx 1.6156$, $k_{50^\circ\text{C}} \approx 0.6157$, and $k_{40^\circ\text{C}} \approx 0.2534$ l/mol·s. The reaction temperature coefficient is equal to $\gamma = 2.5$.

From the graph of dependence of hydrosilylation reaction rate constants' logarithm on the reverse

TABLE I
Some Physical-Chemical Properties of Synthesized Oligomers

No.	Yield, %	Catalyst	Reaction temperature, °C	Ratio of initial compounds	% Changing of active $\equiv\text{Si-H}$ groups	η_{sp}^*	$\overset{\circ}{\text{A}}, d_1$	$T_{\text{gr}}, ^\circ\text{C}$
I	85	H_2PtCl_6	60	1 : 35	89	0.10	9.83	-57
I ^a	82	H_2PtCl_6	40	1 : 35	80	0.09	—	—
I ^b	83	H_2PtCl_6	50	1 : 35	82	0.09	—	—
II	88	H_2PtCl_6	60	1 : 70	91	0.10	—	—
II ^a	78	H_2PtCl_6	40	1 : 70	75	0.09	—	-55
II ^b	82	H_2PtCl_6	50	1 : 70	83	0.09	9.82	—
III	90	H_2PtCl_6	60	1 : 105	92	0.10	—	—
IV	91	H_2PtCl_6	80	1 : 140	99	0.10	—	—
V	94	Pt/C	100	1 : 70	85	0.09	—	—
V ^a	92	Pt/C	80	1 : 70	66	0.09	—	—
V ^b	92	Pt/C	90	1 : 70	76	0.09	—	—
VI	91	Karstedt's	90	1 : 70	87	0.09	—	-58
VI ^a	88	Karstedt's	70	1 : 70	80	0.09	9.82	—
VI ^b	88	Karstedt's	80	1 : 70	82	0.09	—	—

T_{gr} , glass-transition temperature.

^a In 1% solution of toluene, at 25°C.

^b Interchain distances.

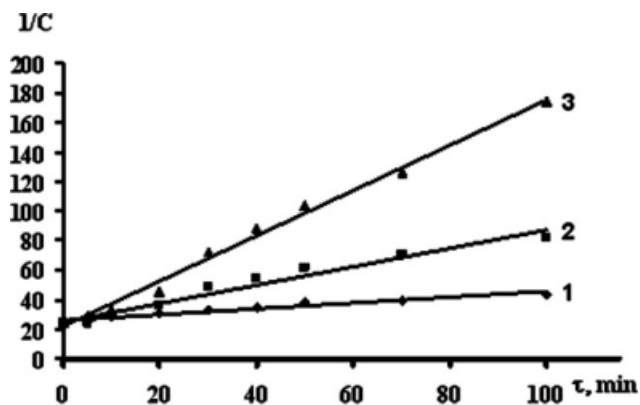


Figure 2 Dependence of inverse concentration on the time during the hydrosilylation reaction of methylhydrosiloxane to 4-vinyl-1-cyclohexene. Where, curve 1 is at 60°C, curve 2 at 50°C, and curve 3 at 40°C.

temperature the activation energy of hydrosilylation reaction was calculated, which is equal to $E_{act} \approx 16,1$ kJ/mol.

We have also studied hydrosilylation reactions of PMHS with 4-vinyl-1-cyclohexene in the presence of platinum hydrochloric acid (0.1 M in THF) with 1 : 105 ratios of initial compounds (1 : 3 stoichiometric ratio with respect to $\equiv\text{Si-H}$ bonds). In case of triple excess of 4-vinyl-1-cyclohexene reaction proceeds with $\sim 92\%$ conversion of active $\equiv\text{Si-H}$ bonds, this results are close to the results in case of double excess of 4-vinyl-1-cyclohexene. In the case of 1 : 140 ratio (1 : 4 stoichiometric ratio between initial compounds with respect to $\equiv\text{Si-H}$ bonds) results in 99% conversion of active $\equiv\text{Si-H}$ bonds.

Hydrosilylation reactions of PMHS with 4-vinyl-1-cyclohexene in the presence of platinum on the charcoal at the same temperatures as in case of H_2PtCl_6 proceed with low rate and depth ($\sim 50\%$). Because of this Pt/C, we have chosen temperature range 80–100°C. At 80°C conversion of active $\equiv\text{Si-H}$ bonds is equal to 66% (oligomer V¹) and at 100°C—87% (oligomer V).

Hydrosilylation reactions of PMHS with 4-vinyl-1-cyclohexene in the presence of Karstedt's catalyst at 60°C proceed with high degree of conversion of active $\equiv\text{Si-H}$ bonds—85% (oligomer VI), but the activity of the catalyst is less than in case of H_2PtCl_6 .

As we already mentioned above, during the hydrosilylation reactions of PMHS with 4-vinyl-1-cyclohexene, the decreases of active $\equiv\text{Si-H}$ groups' concentrations with time were observed. Not all active $\equiv\text{Si-H}$ groups participate in hydrosilylation reactions in spite of the excess of 4-vinyl-1-cyclohexene. Figure 3 shows the dependence of concentrations of active $\equiv\text{Si-H}$ groups on time during hydrosilylation reactions in the presence of different catalysts.

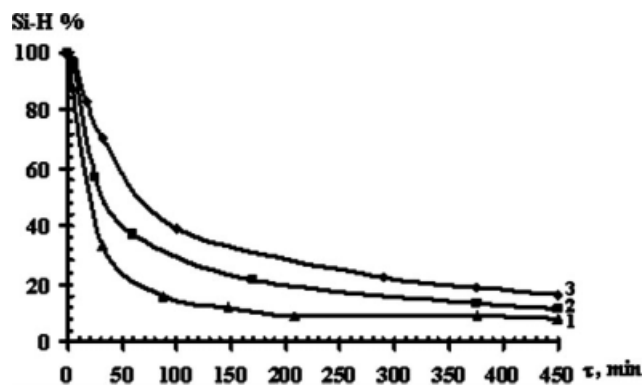


Figure 3 Dependence of changes of concentration of active $\equiv\text{Si-H}$ groups on the time, upon hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydrosiloxane with 4-vinyl-1-cyclohexene, where curve 1 represents the values obtained at 60°C with 1 : 70 ratio in the presence of H_2PtCl_6 , curve 2 represents the values obtained at same conditions in the presence of Karstedt's catalyst and curve 3 represents the values in the presence of Pt/C at 100°C.

Comparison was done for optimal conditions of reactions, for H_2PtCl_6 and Karstedt's catalysts it was 60°C, but for Pt/C it was 100°C, here, we want to mention that in the presence of Pt/C at 60°C reaction does not proceed. Figure 3 evidently shows the influence of the catalysts on the reaction rate and on conversion of active $\equiv\text{Si-H}$ groups. From the Figure 3, we can conclude that the activity of catalysts for hydrosilylation reactions of PMHS with 4-vinyl-1-cyclohexene decreases in the next rank: $\text{H}_2\text{PtCl}_6 >$ Karstedt's catalyst $>$ Pt/C.

Figure 4 shows FTIR spectra of oligomer I. From the literature, it is known that hydrosilylation of 4-vinyl-1-cyclohexene proceeds only with vinyl fragment.^{18,25,26} In contrast to literature data,¹⁴ we have established from FTIR spectra that hydrosilylation of PMHS with 4-vinyl-1-cyclohexene proceeds also with participation of unsaturated bond of cyclic fragment. We observe absorption bands characteristic for asymmetric valence oscillation of linear

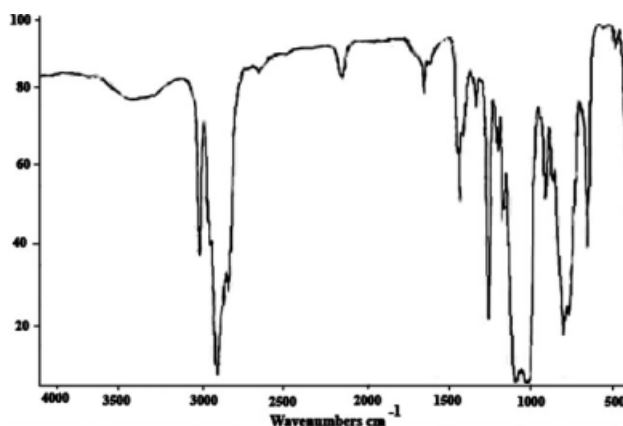


Figure 4 FTIR spectrum of oligomer I.

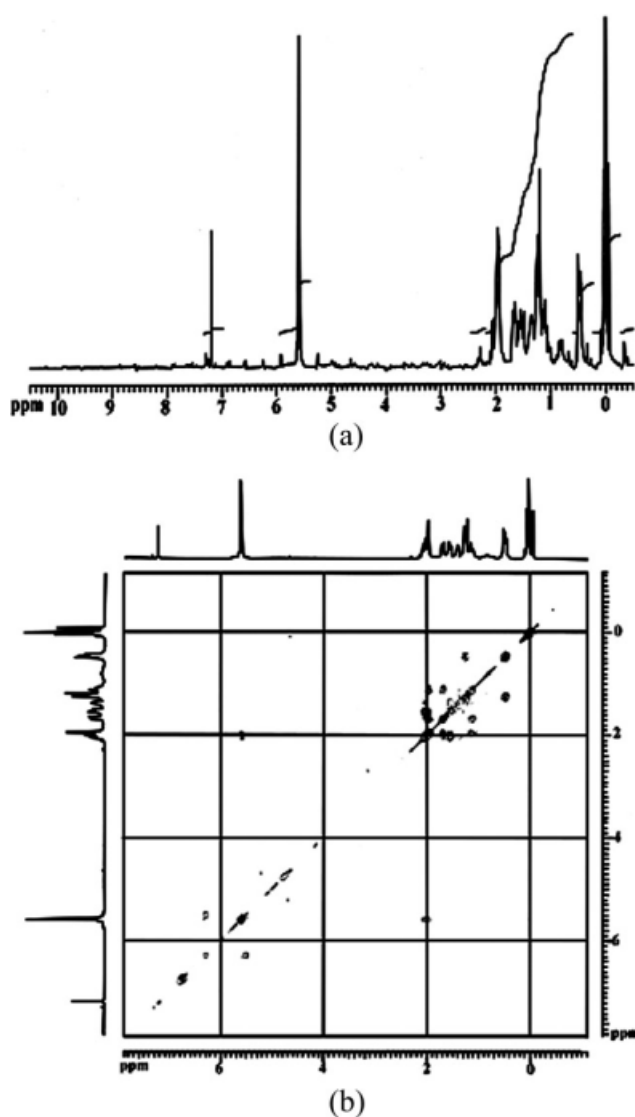


Figure 5 ^1H and H,H-COSY NMR spectra of oligomer I.

$\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds at 1025 cm^{-1} . In the 840 and 1257 cm^{-1} regions, we observe the absorption bands characteristic for $-\text{OSiMe}_3$ and $\equiv\text{Si}-\text{Me}$ accordingly. Absorption band in the 1650 cm^{-1} region characteristic for $-\text{CH}=\text{CH}-$ bonds of cyclic fragment proves that reaction proceeds with substituted vinyl group. In addition, we observe an absorption band in the region 2165 cm^{-1} characteristic for unreacted $\equiv\text{Si}-\text{H}$ bonds. In the spectra, one can observe signal in the $2846\text{--}2915\text{ cm}^{-1}$ region characteristic for cyclohexane fragment, which proves that reaction proceeds with participation of unsaturated bond of cyclic fragment.

In Figure 5, we show ^1H and H,H-Cosy NMR spectrum of oligomer I, where one can observe singlet signals for protons in $\equiv\text{SiMe}$ and SiMe_3 groups with chemical shifts $\delta \approx 0.01\text{ ppm}$ and $\delta \approx 0.03\text{ ppm}$. In spectra, one can observe signals $\delta \approx 0.45$ and $\delta \approx 1.2\text{ ppm}$ characteristic for methylene

protons accordingly in $\equiv\text{SiCH}_2-$ and $\text{C}_6\text{H}_9\text{CH}_2-$ fragments. This shows that reaction proceeds by participation of vinyl group. In the spectra, one can observe signals with low intensities with chemical shifts $\delta \approx 0.8$ and $\delta \approx 1.35\text{ ppm}$ accordingly characteristic for methyl protons and methine protons in $=\text{CH}-\text{CH}_3$ fragment. These two signals with low intensities show that reaction proceeds according to the Markovnikov rule with low degree. Signals with chemical shifts $\delta \approx 1.5$, 1.7 and 2.0 ppm correspond to methylene protons of cyclohexene. Signal with centre of chemical shift $\delta \approx 5.65\text{ ppm}$ corresponds to $-\text{CH}=\text{CH}-$ methine protons of cyclic fragment. In the spectra, one can observe multiple signals with low intensities with the centre of chemical shifts $\delta \approx 5.0$ and 5.8 ppm characteristic for methylene and methine protons of vinyl group, this proves that hydride addition proceeds toward double bond in the cyclic fragment.

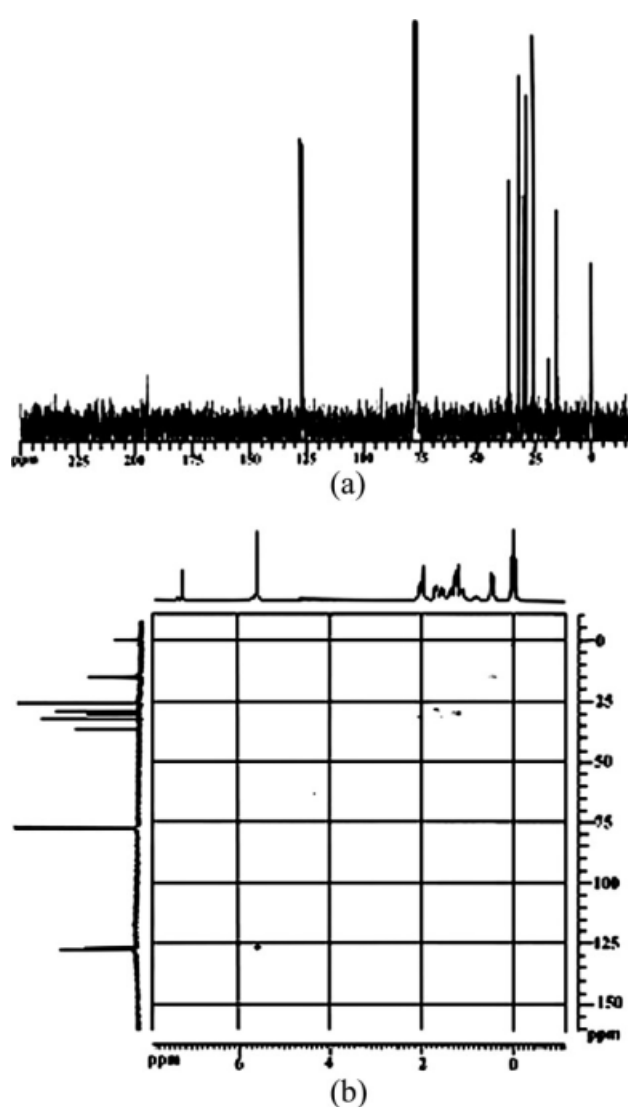
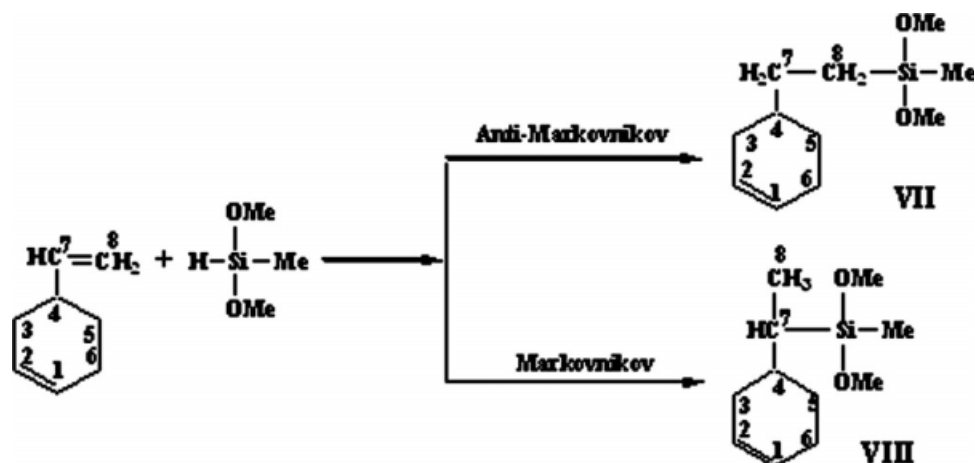


Figure 6 ^{13}C and C,H-correlation NMR spectra of oligomer I.



Scheme 5 Modeling hydrosilylation reaction of methyltrimethoxysilane with 4-vinyl-1-cyclohexene according to the anti-Markovnikov and Markovnikov rule.

^{13}C and C,H-correlation NMR spectra of oligomer I (Fig. 6) is in full correlation with ^1H and H,H-COSY NMR spectra of oligomer I and proves that reaction proceeds according to anti-Markovnikov and Markovnikov rule. In the ^{13}C NMR spectra one can observe signals $\delta \approx 0.01$ and $\delta \approx 0.29$ ppm characteristic for carbon atoms in $\equiv\text{SiMe}$ and $-\text{SiMe}_3$ fragments, signal $\delta \approx 14.98$ ppm for

$\equiv\text{SiCH}_2-$ fragment, signal $\delta \approx 25.68$ ppm for methine carbon in $=\text{CH}-\text{CH}_3$, also signals $\delta \approx 126.91$ and $\delta \approx 127.32$ ppm characteristic for methine carbons of cyclic $-\text{CH}=\text{CH}-$ fragment. In the spectra, one can also observe signals $\delta \approx 28.94$, 30.01, 30.10, 31.98, and 36.68 ppm for methine and methylene carbon atoms of cyclic fragment. C,H-correlation NMR spectra of oligomer I is in full correlation with ^1H NMR and ^{13}C NMR spectrum data.

Determination of the ratio of the fragments obtained from the anti-Markovnikov and Markovnikov rules, and also from hydride addition with double bond of cyclic fragment, is not available, because the spectra have complicated structure.

We have performed calculations using a quantum-chemical semi empirical AM1 method²⁷ for modeling reaction between methyltrimethoxysilane [$\text{Me}(\text{MeO})_2\text{SiH}$] and 4-vinyl-1-cyclohexene for full characterization of hydride addition of PMHS to 4-vinyl-1-cyclohexene using software Chem3D Ultra 9.0 from Cambridge Soft. Calculations were carried out according to the method discussed by us in our previous work.²⁸

We have considered the hydrosilylation of [$\text{Me}(\text{MeO})_2\text{SiH}$] with 4-vinyl-1-cyclohexene on vinyl group according to anti-Markovnikov and Markovnikov rules and also hydrosilylation with double bond of the cyclic fragment.

First, we have made calculations of the hydrosilylation reaction of modeling compound methyltrimethoxysilane [$\text{Me}(\text{MeO})_2\text{SiH}$] with 4-vinyl-1-cyclohexene

according to the anti-Markovnikov and Markovnikov rule. The modeling reaction proceeds according to the following Scheme 5 with formation of compound VII and VIII, respectively:

The distance $R_{\text{C-Si}}$ between the double bonded carbon atoms C_8 or C_7 and silicon was assumed 1.0 Å longer than the bond length as expected in the product. The change of the distance $R_{\text{C-Si}}$ between the atom of silicon and the double bonded carbon atom was about 0.05 Å. The change of energy (ΔH) calculated from AM1 as a function of the distance $R_{\text{C-Si}}$ is presented in Figure 7 (curves 1 and 2).

We have also considered the hydrosilylation reaction of modeling compound methyltrimethoxysilane [$\text{Me}(\text{MeO})_2\text{SiH}$] with 4-vinyl-1-cyclohexene toward $-\text{CH}=\text{CH}-$ double bond in the cyclic fragment. Here, we want to mention that from the literature

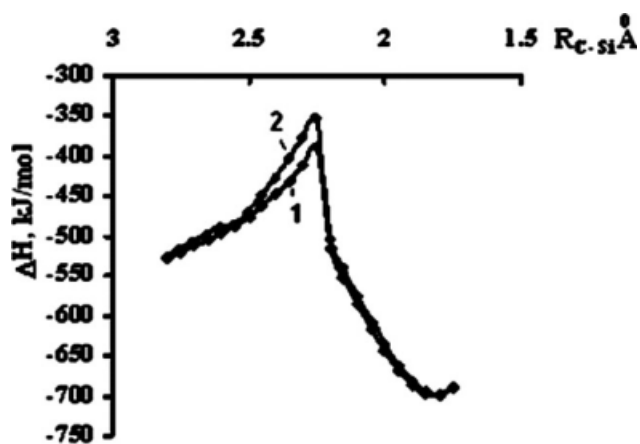
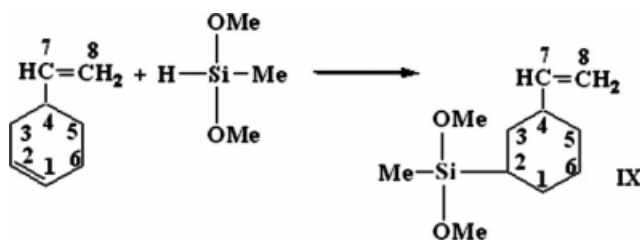


Figure 7 The change of energy (ΔH) as a function of the distance $R_{\text{C-Si}}$ between silicon and double bonded carbon atoms in modeling hydrosilylation reaction of methyltrimethoxysilane with 4-vinyl-1-cyclohexene according to anti-Markovnikov rule (curve 1) and Markovnikov rule (curve 2).



Scheme 6 Modeling hydrosilylation reaction of methyldimethoxysilane with 4-vinyl-1-cyclohexene at 1-2 position.

this direction is considered as not available. The model reaction proceeds according to the following Scheme 6 with formation of compound IX.

The curve of the change of energy (ΔH) calculated from AM1 as a function of the distance R_{C-Si} was done according to above considered method and it is presented in Figure 8.

It must be noted that activation energies and heats of formation in modeling reaction of hydrosilylation of methyldimethoxysilane to 4-vinyl-1-cyclohexene during 2-1 addition approximately is the same.

Using the modeling reactions, we have calculated activation energies E_{act} and the heats of formation (ΔH) of the hydrosilylation products. One can observe that ΔH monotonously decreases with decreasing distance while strengthening of newly formed bonds takes place. Activation energies for the modeling reactions were calculated from the difference of the maxima and the initial points from Figures 7 and 8. Table II presents activation energies and heats of formations for all three directions.

Comparison of activation energies and heats of formations shows that reaction may proceed according to all three directions. Energetically most favourable directions for modeling hydrosilylation reaction of methyldimethoxysilane with 4-vinyl-1-cyclohexene

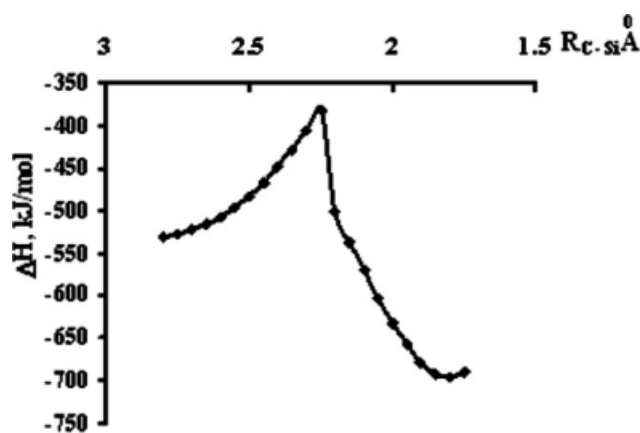


Figure 8 The change of energy (ΔH) as a function of the distance R_{C-Si} between silicon and carbon atoms in modeling hydrosilylation reaction of methyldimethoxysilane with 4-vinyl-1-cyclohexene toward double bond in the cyclic fragment.

TABLE II
Heats of Formations and Activation Energies for Modeling hydrosilylation Reaction of Methyldimethoxysilane with 4-vinyl-1-Cyclohexene

Reaction direction	Heat of formation, ΔH kJ/mol	Activation energy, E_{act} kJ/mol
Anti-Markovnikov rule	-172.0	136.7
Markovnikov rule	-166.6	142.7
Hydrosilylation towards the double bond of cyclic fragment (1-2 addition)	-164.2	149.0

can be listed in descending order as follows: anti-Markovnikov rule, Markovnikov rule, and reaction with double bond of cyclic fragment. The results of theoretical calculations are in good agreement with NMR spectral data.

The synthesized oligomers were studied by GPC method. Figure 9 shows the molecular weight distribution of oligomer III. From which it is evident that oligomer III has bimodal molecular weight distribution. Its molecular weight is equal to: $\overline{M}_n \approx 1,36 \times 10^4$, $\overline{M}_w = 2,51 \times 10^4$, $D = 1.85$.

As it is obvious, the average molecular weights of synthesized oligomers several times exceed theoretical values of molecular weights calculated in case of full hydrosilylation. It indicates that during intermolecular hydrosilylation reaction branching process also takes place.

It must be noted that oligomer III additionally was heated for 4-5 hours at 80°C temperature and at this time the inter-molecular hydrosilylation takes place and in organic solvents practical insoluble polymer is obtained. Thus, synthesized oligomers are thermoreactive systems where cross-linking reactions proceeds with participation of the catalyst remainder in system.

Synthesized oligomers were investigated by DSC analyses. For oligomer I, there is only single endothermic peak which corresponds to the glass

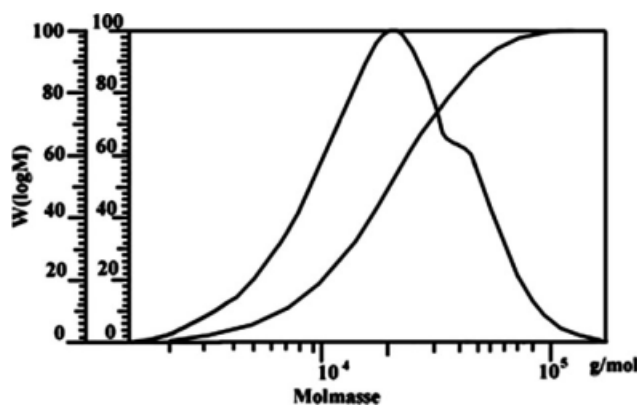


Figure 9 Gel-permeation chromatographic curves of oligomer III.

transition temperature and is equal to $T_g \approx -57^\circ\text{C}$. Glass transition temperature of the oligomer I is close to the value of glass transition temperatures of the products of hydrosilylation reactions of PMHS with styrene (-50°C), α -styrene (-56°C).²⁴

We have performed wide-angle X-ray scattering analysis for obtained oligomers. It was shown that the oligomer I is one-phase amorphous system. Diffraction patterns display two maxima. The main one corresponds to the maximum of the interchain distance d_1 whereas the second maximum corresponds to d_2 , which characterizes both intramolecular and interchain interactions.²⁹

CONCLUSION

Hydrosilylations of α,ω -bis(trimethylsiloxy)methylhydrosiloxane with 4-vinyl-1-cyclohexene in the presence of a catalyst were performed at various temperatures and thermoreactive methylsiloxane oligomers with unsaturated side groups in the side chains have been obtained. It was shown that the reaction proceeds according to anti-Markovnikov rule, Markovnikov rule, and with double bond of cyclic fragment.

The synthesised oligomer I was used for preparation of siliconorganic rubbers, it gives cross linked systems during heating without addition of catalysts. The obtained oligomer contains reactionable unsaturated bonds and after addition of 3–5 mass % of sulphur and heating it easily gives 3D structures.

References

1. Yilgor, I.; Steckle, W. P. Jr.; Yilgor, E.; Freelin, R. G.; Riffle, J. S. *J Polym Sci Part A: Polym Chem* 1989, 27, 3673.
2. Garin, S.; Lecamp, L.; Youssef, B.; Bunel, C. *Eur Polym J* 1999, 35, 473.
3. Hou, S. S.; Chung, Y. P.; Chan, C. K.; Kup, C. P. *Polymer* 2000, 41, 3263.
4. Kricheldorf, H. R. Ed. *Silicon in Polymer Synthesis*; Springer: Berlin, 1996.
5. Chauhan, B. P. S.; Rathore, J. S.; Gllloxhani, N. *Appl Organomet Chem* 2005, 19, 542.
6. Chauhan, B. P. S.; Boudjouk, P. *Tetrahedron Lett* 2000, 41, 1127.
7. Coquert, X.; El Achari, A.; Hajaiej, A.; Lablache-Combier, A.; Loucheux, C.; Randrianarisoa, L. *Macromol Chem* 1991, 192, 1517.
8. Titvinidze, G.; Tatrishvili, T.; Mukbaniani, O. *Georgian Chem J*, 2005, 5, 249.
9. Yao, D.-S.; Zhang, B.-Y.; Sun, Q.-J.; Zhang, L.-F. *J Appl Polym Sci*, 2005, 95, 946.
10. Chien, L.-C.; Cada, L. G. *Macromolecules* 1994, 27, 3721.
11. Belfield, K. D.; Chinna, C.; Najjar, O. *Macromolecules* 1998, 31, 2918.
12. Touloukhonova, I.; Bjerke-Kroll, B.; West, R. *J Organomet Chem* 2003, 686, 101.
13. Hua, J.; Li, Z.; Long, K.; Qin, J.; Li, Sh.; Ye, Ch.; Lu, Z. *J Polym Sci Part A: Polym Chem* 2005, 43, 1317.
14. Petrov, A. D.; Ponomarenko, V. A.; Sokolov, B. A.; Odobashian, G. V. *Bull Acad Sci USSR, Div Chem Sci*, 1957, 10, 1206.
15. Speier, J. L.; Webster, J. A.; Barnes, G. H. *J Am Chem Soc*, 1957, 3, 974.
16. U.S. Pat. 2601913 (1976). C.A., 1977, 86, 43809.
17. U.S. Pat. 6245925 (2001).
18. Iuriev, V. P.; Salimgarieva, I. M.; Kaverin, V. V.; Tolstikov, G. A. *Zh Obshch Khim*, 1977, 47, 355.
19. Ganicz, T.; Mizerska, U.; Moszner, M.; O'Brien, M.; Perry, R.; Sta'nczyk, W. A. *Appl Catal A* 2004, 259, 49.
20. Marciniak, B.; Gulinski, J.; Kopylova, L.; Maciejewski, H.; Grundwald-Wyspianska, M.; Lewandowski, M. *Appl Organomet Chem* 1997, 11, 843.
21. Iwahara, T.; Kusakabe, M.; Chiba, M.; Yonezawa, K. *J Polym Sci A* 1993, 31, 2617.
22. Mukbaniani, O.; Titvinidze, G.; Tatrishvili, T.; Mukbaniani, N.; Brostow, W.; Pietkiewicz, D. *J Appl Polym Sci* 2007, 104, 1176.
23. Mukbaniani, O.; Tatrishvili, T.; Titvinidze, G.; Mukbaniani, N.; Lezhava, L.; Gogeshvili, N. *J Appl Polym Sci* 2006, 100, 2511.
24. Mukbaniani, O.; Tatrishvili, T.; Titvinidze, G.; Mukbaniani, N. *J Appl Polym Sci* 2006, 101, 1388.
25. Yuriev, V. P.; Salimgareva, I. M. *Hydrosilylation Reactions of Olefins*; Nauka: Moscow, 1982, p 76 (in Russian).
26. Yuriev, V. P.; Salimgareva, I. M.; Zhebarov, O. Zh.; Kaverin, V. V.; Rafikov, S. S. *Dokl Akad Nauk* 1976, 229, 892 (in Russian).
27. Dewar, M. I. S.; Zeobish, E. G.; Healy, E. F.; Stewart, J. S. *J Am Chem Soc* 1985, 107, 3902.
28. Mukbaniani, O.; Tatrishvili, T.; Titvinidze, G.; Mukbaniani, N.; *J Appl Polym Sci* 2006, 101, 388.
29. Mukbaniani, O. V.; Zaikov, G. E. *Cycloliner Organosilicon Copolymers: Synthesis, Properties, Application*; VSP: Utrecht, The Netherlands; Boston, MA, 2003.