

Synthesis and Characterization of Polysiloxanes with Pendant Bicyclic Fragments

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ABSTRACT: The hydrosilylation reactions of 5-vinyl-2-norbornene with α,ω -bis(trimethylsiloxy)methylhydrosiloxane catalyzed by platinum hydrochloric acid (0.1M solution in tetrahydrofuran), Karstedt's catalyst ($\text{Pt}_2[(\text{VinSiMe}_2)_2\text{O}]_3$) and platinum on the carbon have been studied. Dependence of reaction rate and active $\equiv\text{Si}-\text{H}$ bonds' conversion depth on the catalyst was investigated. Even in the excess of the 5-vinyl-2-norbornene, not all active $\equiv\text{Si}-\text{H}$ groups participate in the hydrosilylation reaction. The reaction order, activation energies, and rate constants have been determined for hydrosilylation reactions in the presence of H_2PtCl_6 . The synthesized oligomers were characterized by Fourier transform

infrared spectroscopy (FTIR), ^1H , ^{13}C , $^1\text{H}-^1\text{H}$ correlation spectroscopy (COSY), and C,H-correlation NMR spectroscopy. Synthesized polysiloxanes were characterized by wide-angle X-ray, gel-permeation chromatography, and DSC analyses. Calculations using the quantum-chemical semi-empirical AM1 method for modeling reaction between methyltrimethoxysilane $[\text{Me}(\text{MeO})_2\text{SiH}]$ and 5-vinyl-2-norbornene were performed to evaluate possible reaction paths. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1572–1582, 2011

Key words: polysiloxanes; oligomers; crosslinking; kinetics; synthesis; hydrosilylation

INTRODUCTION

Hybrid organic–inorganic materials, where molecular organic and inorganic fragments are combined, have been considered potentially attractive for the purpose of developing new materials with a broad spectrum of interesting properties. In comparison with organic and inorganic constituents and polymers separately, hybrid organic–inorganic materials have a lot of advantages.^{1–5}

Polysiloxanes find numerous applications in different fields of chemistry and engineering. All of these applications rely on the unique physical and chemical properties of silicones. Widely applied hydrosilylation of polymeric systems^{6,7} and especially hydrosilylative curing of polyvinylsiloxanes by polyhydrogenesiloxanes have attracted great interest due to the practical outcome and recent development in silicon-containing polymeric systems. From aforementioned, it is evident that synthesis and investigation of new polysiloxanes with double bond containing fragments attracts much attention due to their wide applications.

The hydrosilylation process is the most widely used method for preparation of organofunctional polymethylsiloxanes from poly(methylhydro)siloxanes.^{8,9}

Transition metal catalyzed hydrosilylation of organic substrates possessing unsaturated carbon–carbon bond is an effective, still attractive and most important commercial way of synthesis of carbon-functional silanes, siloxanes, and oligo(poly)siloxanes.^{6,7,10} Since Speier's first discovery that H_2PtCl_6 is an efficient hydrosilylation catalyst,¹¹ the effect of different catalysts on the hydrosilylation process has been extensively studied.¹²

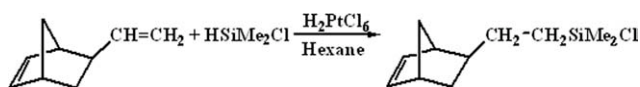
From Ref. 13, it is known that addition of dimethylchlorosilane to the mixture endo- and exo-isomer forms of 5-vinyl-2-norbornene in the presence Rhodium catalysts, the reaction proceeds on the vinyl group according to the following Scheme 1.

Hydrosilylation of methylhydrochlorosilane with 5-vinyl-2-norbornene in the presence of Spier catalyst proceeds both on vinyl group with obtaining of [2-(2-norbornene-5-yl)ethyl]methylchlorosilane (65%) as well as on unsaturated bond in bicyclic fragment with obtaining of 5-vinyl norbornene-2-yl methyl chlorosilane (35%), according to the following Scheme 2.¹³

The hydrosilylation reaction of 5-vinyl-2-norbornene with HSiEt_2Me in the presence of Rhodium catalyst gave only products (a and b) arising from the endo starting material, Scheme 3.¹⁴

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Scheme 1 Hydrosilylation of dimethylchlorosilane with 5-vinyl-2-norbornene in the presence of Spier catalyst.

The presence of byproduct **b** indicated that an intramolecular hydrogen transfer took place to some extent when the diene had a strongly coordinating site such as a norbornene moiety.

In this work, we have studied modification of PMHS via hydrosilylation reactions in the presence of platinum catalysts, which are reported to be among the most active catalysts for hydrosilylation reactions.¹² We have investigated the dependence of reaction rate and active $\equiv\text{Si}-\text{H}$ bonds' conversion depth on the catalyst.

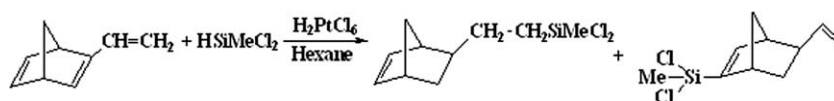
EXPERIMENTAL

Materials

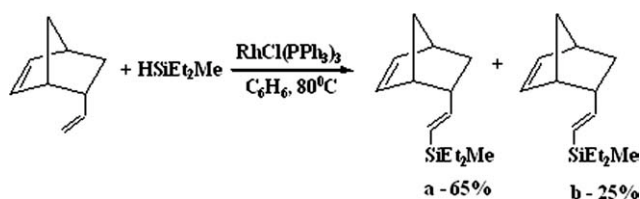
Polymethylhydrosiloxane ($n = 35$) (Aldrich), platinum hydrochloric acid (Aldrich), Karstedt's catalyst ($\text{Pt}_2[(\text{VinSiMe}_2)_2\text{O}]_3$) or platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (solution in polydimethylsiloxane [PDMS]), platinum on the carbon and 5-vinyl-2-norbornene (Aldrich) were used as received (a 78 : 22 mixture of endo- and exo-isomers). Toluene was dried over and distilled from sodium under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Platinum hydrochloric acid (0.1M solution) in THF was prepared and kept under nitrogen at low temperature.

Characterization

FTIR spectra were recorded on a Nicolet Nexus 470 machine with mercury cadmium telluride (MCT) B-type detector (MCTB). ^1H , $^1\text{H}-^1\text{H}$ COSY, ^{13}C -NMR, and $^1\text{H}/^{13}\text{C}$ -correlation NMR spectra were recorded on a 500 MHz Bruker NMR spectrometer, using CDCl_3 as the solvent and an internal standard. 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



Scheme 2 Hydrosilylation of methylhydrochlorosilane to 5-vinyl-2-norbornene in the presence of Spier catalyst.



Scheme 3 Hydrosilylation of methyl-diethylsilane with 5-vinyl-2-norbornene in the presence of Rhodium catalyst.

the peaks. The heating and cooling scanning rates were 10 K min^{-1} .

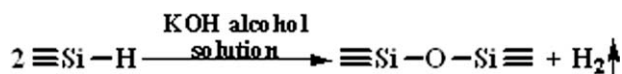
Gel-permeation chromatographic investigation was carried out with the use of Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å ultrastryragel columns. Sample concentration was $\sim 3\%$ by weight in toluene and typical injection volume for the siloxane was $5\text{-}\mu\text{L}$ flow rate— 1.0 mL min^{-1} . Standardization of the GPC was accomplished by the use of styrene or polydimethylsiloxane standards with the known molecular weight.

Wide-angle X-ray analyses were performed on a DRON-2 (Burevestnik, St. Petersburg, Russia) instrument. A-CuK_α was measured without a filter; the angular velocity of the motor was $\omega \approx 2^\circ/\text{min}$.

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

The content of active $\equiv\text{Si}-\text{H}$ groups in oligomers was calculated on the basis of the following reaction Scheme 4.

In a two-necked flask an exactly weighed amount of $\equiv\text{Si}-\text{H}$ containing oligomer was placed, which should correspond to evolution of certain volume of hydrogen gas. The pressure equalized dropping funnel with 0.5M KOH alcohol solution onto the flask was fitted. The flask with a gas burette and with a leveling bottle at the bottom part was connected, by means of a silicon tube. The system was allowed to stand for 10 min. The water level in the leveling bottle adjusts to the same level as that in the gas burette (V_1 , mL) is recorded. After, the 0.5M KOH alcohol solution was added slowly. As hydrogen gas evolves, the water level goes downward. The both water levels were kept the same as each other so that it was possible to equalize the pressure in the system to atmosphere. After the evolution of hydrogen gas completes (around 3–5 min) another 5 min later, the value of the water level in the burette (V_2 ,



Scheme 4 Reaction scheme of potassium hydroxide with hydrosilanes.

mL) were recorded. The difference between V_2 and V_1 gives the volume of eliminated hydrogen gas (V , mL). The Si—H content of an oligomer is given by the following:

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

where p is the atmospheric pressure at measurement (atm), V is the gas volume captured (mL), W is the sample weight (g), $R = 0.0082$ (gas constant) (L atm mol⁻¹ K⁻¹), and T is the temperature (K at measurement).¹⁵

Hydrosilylation reaction of PMHS with 5-vinyl-2-norbornene in the presence of H₂PtCl₆

Polymethylhydrosiloxane (0.9850 g, 0.435 mmol), 5-vinyl-2-norbornene (1.8287 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. Then the catalyst, 0.1M solution of platinum hydrochloric acid in THF ($5 \div 9 \times 10^{-5}$ g per 1.0 g of starting substance), was introduced. After the reaction completed, the solvent was partially evaporated, the reaction product was precipitated from toluene solution by *n*-hexane, and 2.15 g (86%) oligomer was obtained. The hydrosilylation reactions in the presence of other catalysts were carried out according to the aforementioned method.

RESULTS AND DISCUSSION

There is sufficient literature data on hydrosilylation of norbornene.¹⁶ For example, the hydrosilylation of norbornene with HSiCl₃ takes place under mild conditions in the presence of an optically active 2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MeO-MOP) complex of palladium to produce exo-2-(trichlorosilyl)norbornane with 99% quantitative yield.^{17,18}

5-Vinyl-2-norbornene contains two active double bonds, which can participate in hydrosilylation reactions. Thus, hydrosilylation reaction can proceed into two main directions: with substituted vinyl group and with double bond in bicyclic fragment. With vinyl group, hydride addition can proceed according to anti-Markovnikov and Markovnikov rule.

For the purpose to synthesize new functional polysiloxanes with pendant bicyclic fragments including unsaturated bonds, we have carried out hydrosilylation reactions of α,ω -bis(trimethylsiloxy)-

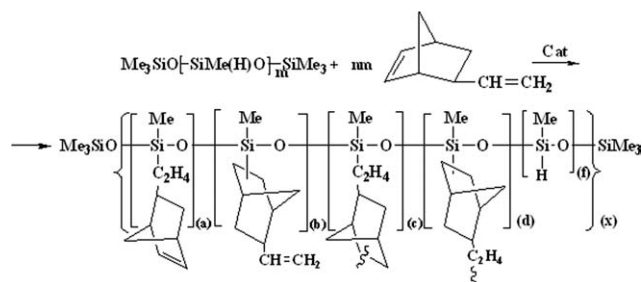
methylhydrosiloxane with 5-vinyl-2-norbornene in the presence of platinum hydrochloric acid (0.1M solution in THF), Karstedt's catalyst (Pt₂[(VinSiMe₂)₂O]₃ in PDMS) and platinum on the charcoal. To achieve higher conversion of active $\equiv \text{Si}-\text{H}$ bonds reactions were carried out with various molar ratios of initial compounds (1 : 35, 1 : 70, and 1 : 105). From the Refs. 19 and 20, it is known that not all active $\equiv \text{Si}-\text{H}$ groups participate in hydrosilylation reactions in case of stoichiometric relationships with respect to $\equiv \text{Si}-\text{H}$ bonds.

Preliminary heating of initial compounds in the temperature range of 20–60°C in the presence of catalysts showed that in these conditions polymerization of 5-vinyl-2-norbornene and destruction of siloxane backbone does not take place. No changes in the NMR and FTIR spectra of initial compounds were found.

We have carried out aforementioned reactions without solvent, but reactions proceed vigorously (especially in case of platinum hydrochloric acid and Karstedt's catalyst) and at initial stages of conversion of $\equiv \text{Si}-\text{H}$ bonds ($\sim 25\%$) gelation takes place via intermolecular hydrosilylation. To prevent gelation and to investigate kinetic parameters of the reaction, we have carried out hydrosilylation in dry toluene solution.

In general, hydrosilylation of α,ω -bis(trimethylsiloxy)methylhydrosiloxane to 5-vinyl-2-norbornene proceeds by the following Scheme 5. Where: [(a) + (b) + (c) + (d) + (f)](x) = $m \approx 35$; Cat.—H₂PtCl₆·6H₂O—20°C (I1), 30°C (I2), and 40°C (I) (ratio 1 : 35), 20°C (II1), 30°C (II2), 40°C (II) (ratio 1 : 70), 20°C (III1), 30°C (III2), 40°C (III) (ratio 1 : 105). Cat.—Pt/C—40°C (IV1), 50°C (IV2), 60°C (IV) (ratio 1 : 70). Karstedt's catalyst- 20°C (V1), 30°C (V2), 40°C (V) (ratio 1 : 70).

The synthesized oligomers are vitreous liquid products, which are well soluble in organic solvents with the specific viscosity $\eta_{sp} \approx 0.08 - 0.1$. Structures and compositions of the oligomers were determined by elemental and functional analyses, FTIR, ¹H, ¹³C, H,H-COSY, and C,H-correlation NMR spectral data. Synthesized polysiloxanes were



Scheme 5 Hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydrosiloxane with 5-vinyl-2-norbornene.

TABLE I
Some Characteristic Data for Hydrosilylation Reaction and Synthesized Oligomers

Oligomer no.	Yield (%)	Catalyst	Reaction temperature (°C)	Ratio of initial compounds	% Conversion of active $\equiv\text{Si-H}$ groups	η_{sp}^a	d_1 (Å)	T_g (°C)
I	86	H_2PtCl_6	40	1 : 35	83	0.09	9.30	-54
I ¹	84	H_2PtCl_6	20	1 : 35	80	0.08	—	—
I ²	85	H_2PtCl_6	30	1 : 35	81	0.08	—	—
II	86	H_2PtCl_6	40	1 : 70	92	0.09	9.31	-52
II ¹	85	H_2PtCl_6	20	1 : 70	82	0.09	—	—
II ²	85	H_2PtCl_6	30	1 : 70	87	0.08	—	—
III	88	H_2PtCl_6	40	1 : 105	95	0.1	9.28	—
III ¹	86	H_2PtCl_6	20	1 : 105	89	0.08	—	—
III ²	87	H_2PtCl_6	30	1 : 105	93	0.09	—	—
IV	90	Pt/C	60	1 : 70	72	0.1	—	—
IV ¹	87	Pt/C	40	1 : 70	69	0.09	—	—
IV ²	89	Pt/C	50	1 : 70	72	0.1	—	—
V	88	Karstedt's	40	1 : 70	95	0.1	9.32	-52.4
V ¹	85	Karstedt's	20	1 : 70	88	0.09	—	—
V ²	86	Karstedt's	30	1 : 70	91	0.09	—	—

^a In 1% toluene solution, at 25°C.

characterized by wide-angle X-ray analyses. Some characteristics for hydrosilylation reaction and synthesized oligomers are presented in Table I.

During the hydrosilylation reaction, decrease of active $\equiv\text{Si-H}$ groups' concentration with the time was observed. The hydrosilylation reaction was performed in dry toluene solution ($C \approx 5.7 \times 10^{-2}$ mol L^{-1}). As it is evident from the Table I, not all active $\equiv\text{Si-H}$ groups participate in hydrosilylation reaction. Figure 1 shows the changes of concentration of active $\equiv\text{Si-H}$ groups in time (determined as described in Section Determination of $\equiv\text{Si-H}$ content) in case of hydrosilylation reactions of PMHS

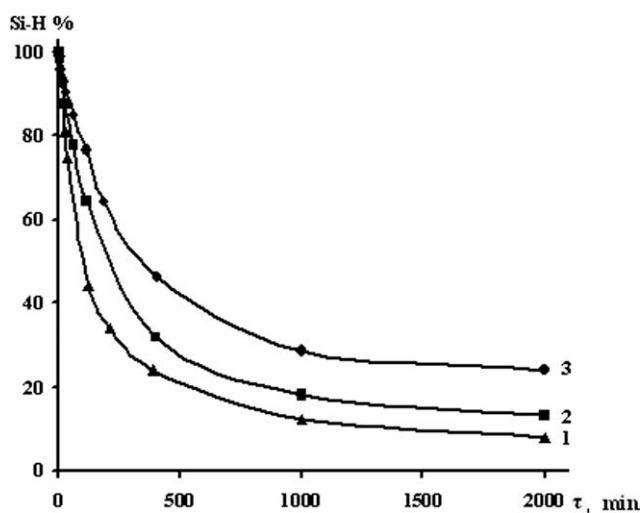


Figure 1 Dependence of changes of concentration of active $\equiv\text{Si-H}$ groups on the time, during hydrosilylation reactions of PMHS with 5-vinyl-2-norbornene, where curve 1 represents the values obtained at 40°C, curve 2 represents the values obtained at 30°C, and curve 3 represents the values obtained at 20°C (Catalyst— H_2PtCl_6).

with 5-vinyl-2-norbornene in the presence of H_2PtCl_6 at 1 : 70 ratios of initial compounds (1 : 2 stoichiometric relationships between initial compounds with respect of $\equiv\text{Si-H}$ bonds). From Figure 1, it is evident that at 20°C hydrosilylation reaction proceeds with $\sim 87\%$ conversion of active $\equiv\text{Si-H}$ groups, whereas at 40°C hydrosilylation reaction proceeds with $\sim 92\%$ conversion. Consequently, with the rise of temperature, the depth of hydrosilylation reaction increases.

Figure 2 shows dependence of the reverse concentration of $\equiv\text{Si-H}$ groups on the time during hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydrosiloxane with 5-vinyl-2-norbornene. One can see that at the initial stages, the hydrosilylation reaction is of second order. From the Refs. 19–21, it is known that hydrosilylation reactions of PMHS with unsaturated compounds as usual at initial stages are of a second order in case of stoichiometric

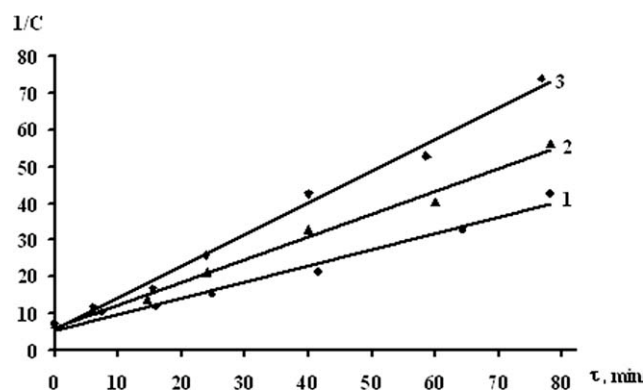


Figure 2 Dependence of reaction rate constants' logarithm on the reverse temperature during hydrosilylation reaction of polymethylhydrosiloxane with 5-vinyl-2-norbornene.

relationships between initial compounds with respect to $\equiv\text{Si}-\text{H}$ bonds. As we can see from experimental results, increasing of concentration of one initial compound do not change reaction order. The reaction rate constants of hydride addition reactions of polymethylhydridesiloxane to 5-vinyl-2-norbornene at various temperatures were determined: $k_{40^\circ\text{C}} \approx 1.5206$, $k_{30^\circ\text{C}} \approx 0.7011$, and $k_{20^\circ\text{C}} \approx 0.3084 \text{ mol L}^{-1} \text{ s}^{-1}$. The reaction temperature coefficient is equal to $\gamma = 2.2$.

We have calculated the activation energy for the reactions using reaction rate constants' logarithm as functions of the reverse temperature. The activation energy is equal to $E_{\text{act}} \approx 20.3 \text{ kJ mol}^{-1}$.

We have also investigated hydrosilylation reactions of polymethylhydrosiloxane with 5-vinyl-2-norbornene in the presence of platinum hydrochloric acid (0.1M solution in THF) with 1 : 105 ratios of initial compounds (1 : 3 stoichiometric relationships between initial compounds with respect to $\equiv\text{Si}-\text{H}$ bonds). In case of triple, excess of 5-vinyl-2-norbornene reaction proceeds deeper than in the case of ratios 1 : 70 of initial components. From the Table I, we can compare results of $\equiv\text{Si}-\text{H}$ bonds' conversion, obtained at same temperatures with different ratios of reacting compounds. From Table I, it is evident that with the increase of concentration of 5-vinyl-2-norbornene reaction proceeds with higher conversion of $\equiv\text{Si}-\text{H}$ bond.

Hydrosilylation reactions of PMHS with 5-vinyl-2-norbornene in the presence of platinum on the charcoal proceed with low rate and depth. Reactions were carried out at higher temperatures than in the case of platinum hydrochloric acid and Karstedt's catalyst, but the conversion of active $\equiv\text{Si}-\text{H}$ bonds was lower (Table I).

Hydrosilylation reaction of polymethylhydrosiloxane with 5-vinyl-2-norbornene in the presence of Karstedt's catalyst at 40°C in the case of 1 : 70 ratio of initial compounds proceeds with high degree of active $\equiv\text{Si}-\text{H}$ bonds conversion $\sim 95\%$ (oligomer V). Here we want to mention that in the presence of H_2PtCl_6 at 40°C temperature in case of 1 : 105 ratio of initial compounds reaction proceeds with the same degree of active $\equiv\text{Si}-\text{H}$ bonds conversion $\sim 95\%$ (oligomers III). It shows superiority of the Karstedt's catalyst in comparison with platinum hydrochloric acid.

During the hydride addition reactions, the changes of active $\equiv\text{Si}-\text{H}$ bonds' concentrations in time were observed. It was shown that not all active $\equiv\text{Si}-\text{H}$ groups participate in hydrosilylation reactions in spite of the excess of 5-vinyl-2-norbornene; it can be explained by steric effect of the pendant bicyclic fragments. In Figure 3, the changes of concentrations of active $\equiv\text{Si}-\text{H}$ groups in time during hydrosilylation reactions in the presence of different

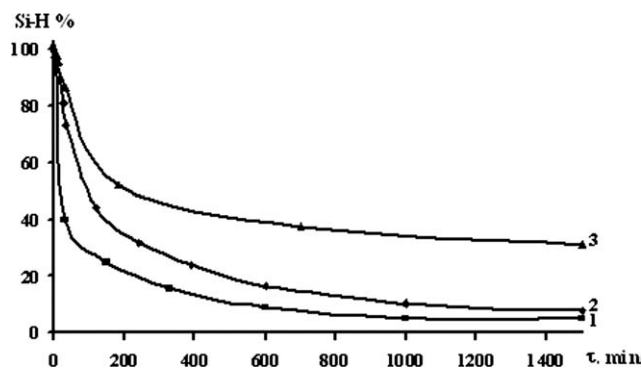


Figure 3 Dependence of changes of concentration of active $\equiv\text{Si}-\text{H}$ groups on the time, during hydrosilylation reaction of PMHS with 5-vinyl-2-norbornene, where curve 1 represents the values obtained at 40°C with 1 : 70 ratio in the presence of Karstedt's catalyst, curves 2 and 3 accordingly represent the values obtained at same conditions in the presence of H_2PtCl_6 and Pt/C at 40°C .

catalysts at 40°C temperature is shown. Figure 3 evidently shows the influence of the catalysts on the reaction rate and depth. From the Figure 3, we can conclude that the activity of catalysts for hydrosilylation reactions of PMHS with 5-vinyl-2-norbornene decreases in the following order: Karstedt's catalyst $>$ H_2PtCl_6 $>$ Pt/C.

In the Figure 4, ^1H and H,H-COSY NMR spectra of oligomer II is given (Fig. 4), where one can observe signals for methyl protons of $\equiv\text{Si}-\text{Me}$ and $-\text{SiMe}_3$ fragments with the chemical shift $\delta = 0.01$ and $\delta = 0.03$ ppm. Signals with chemical shift $\delta \approx 0.45$ and $\delta \approx 2.7$ ppm characteristic accordingly for methylene protons of $\equiv\text{Si}-\text{CH}_2-$ and $\text{C}_7\text{H}_9-\text{CH}_2-$ fragments have low intensities, which shows that reaction according to the anti-Markovnikov rule proceeds with low degree. In the ^1H -NMR spectra, one can observe signals with chemical shift $\delta \approx 0.8$ and $\delta \approx 1.3$ ppm characteristic for methyl protons of $=\text{CH}-\text{CH}_3$ fragment and methyne protons of $=\text{CH}-\text{CH}_3$ fragment accordingly. These two signals show that the reaction proceeds according to Markovnikov rule. From the comparison of intensities of signals characteristic for proceeding of hydrosilylation according to two directions, we can conclude that favorable direction is according to the Markovnikov rule. Multiplet signals with center of chemical shifts $\delta \approx 1.4$, 1.6, 1.95, and 2.4 ppm correspond to methylene and methine protons of norbornene fragment and partially overlapping of resonance signals occurs in exo- and endo-forms of obtained oligomer. In the spectra, one can observe low-intensity multiplet signals with center of chemical shifts $\delta \approx 4.85 \div 5.0$ and $\delta \approx 6.0 \div 6.2$ ppm accordingly characteristic for methylene and methine protons of vinyl groups, this proves that hydrosilylation reaction proceeds at double bond of bicyclic fragment with low degree.

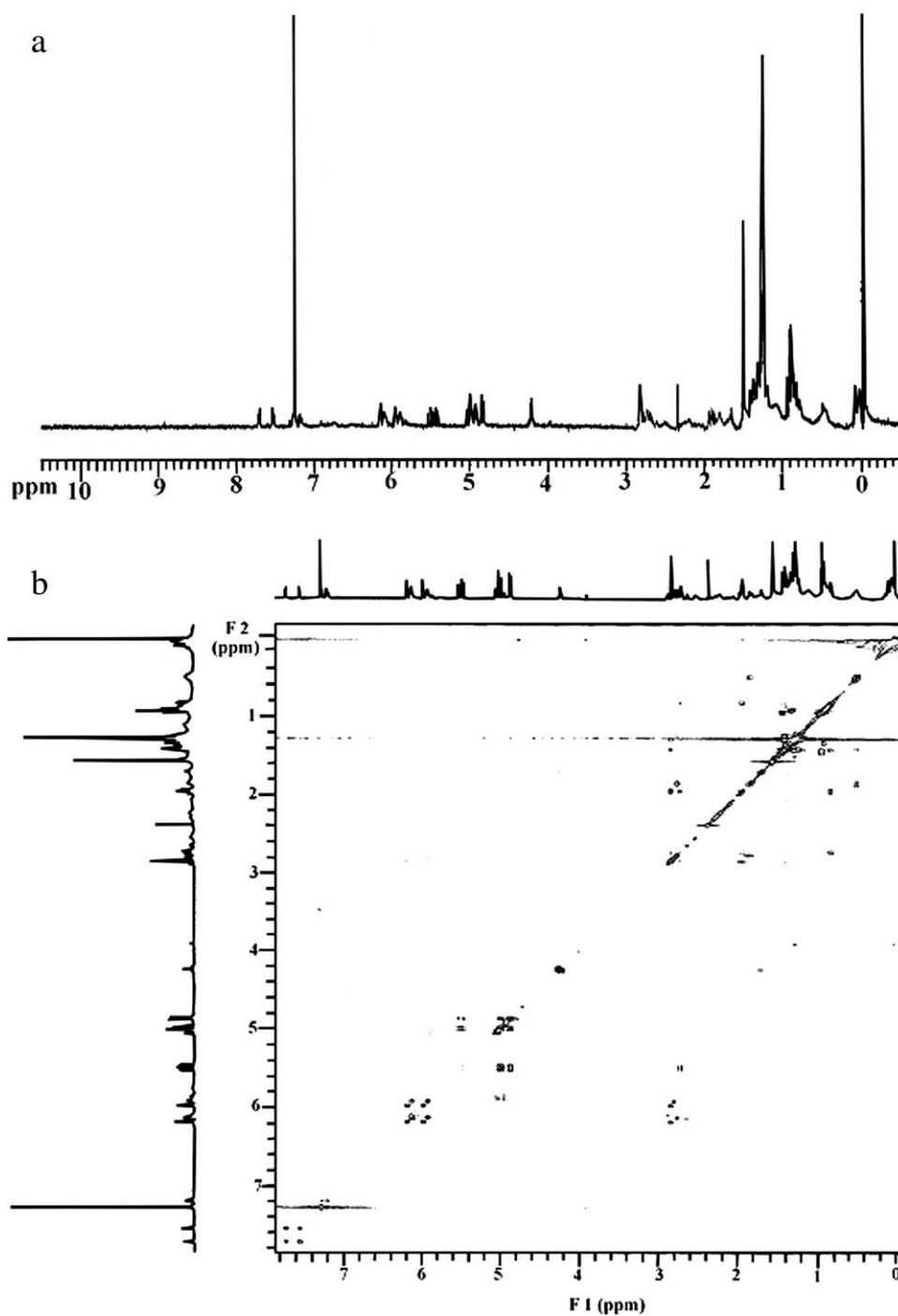


Figure 4 ^1H (a) and H,H-COSY (b) NMR spectra of oligomer II.

Multiplet signal with chemical shift $\delta \approx 5.45 \div 5.55$ ppm corresponds to the methyne protons of $-\text{CH}=\text{CH}-$ fragment. Singlet signal with chemical shift $\delta \approx 4.2$ ppm characteristic for $\equiv\text{Si}-\text{H}$ bond shows that full hydrosilylation does not proceed and that various linked oligomers are obtained.

^{13}C and C,H -correlation NMR spectra of oligomer II (Fig. 5) are in good agreement with ^1H and H,H-COSY NMR spectra as well as proves that reaction proceeds according to all three directions: hydride

addition by Markovnikov and anti-Markovnikov rule, also hydrosilylation by participating of double bond of bicyclic fragment. In the ^{13}C -NMR spectra, one can observe signal $\delta \approx 0.013$ characteristic for carbon atoms in $\equiv\text{SiMe}$ and $-\text{SiMe}_3$ fragments. Signal $\delta \approx 14.04$ ppm characteristic for methylene carbon of $\equiv\text{SiCH}_2-$ fragment and signal $\delta \approx 28.92$ ppm corresponding to methylene carbon in $\text{C}_6\text{H}_5\text{CH}_2-$ proves proceeding of hydrosilylation according to the anti-Markovnikov rule. Signals $\delta \approx$

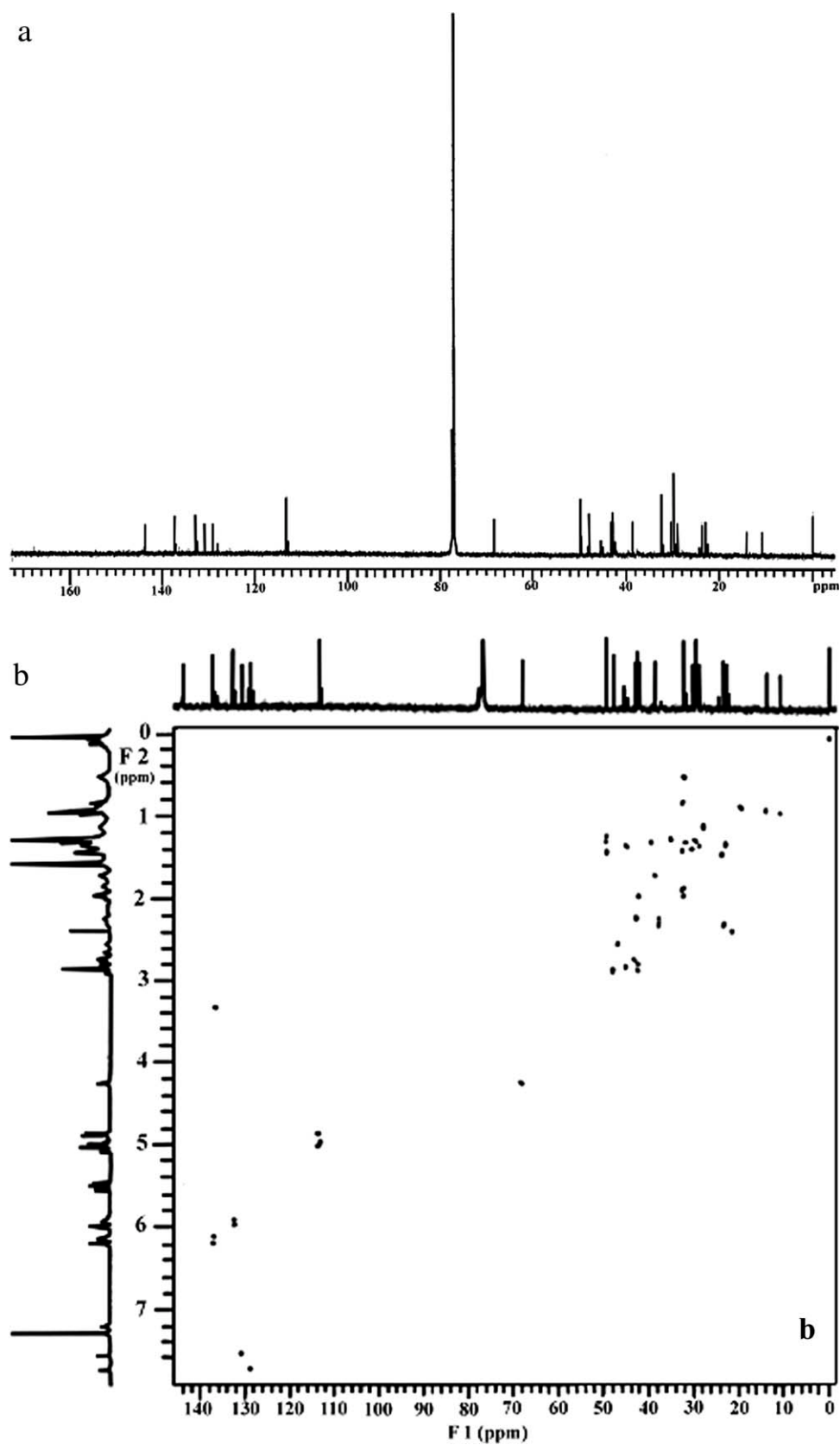


Figure 5 ^{13}C (a) and C,H-correlation (b) NMR spectra of oligomer II.

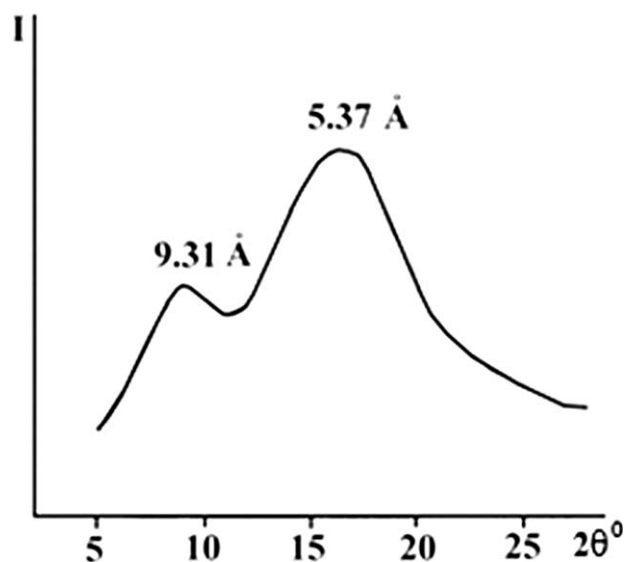


Figure 6 X-ray pattern for oligomer II.

22.98 and $\delta \approx 10.96$ ppm correspond to the methine and methyl carbon atoms in $=\text{CH}-\text{CH}_3$ fragment accordingly and show that the reaction proceeds according to the Markovnikov rule. Signal $\delta \approx 113.12$ ppm corresponds to methylene carbon of vinyl fragment and signal $\delta \approx 143.76$ ppm corresponds to the methyne carbon of the same group. These two signals indicate that hydrosilylation also proceeds with double bond of bicyclic fragment.

To determine the ratio of the fragments obtained from the anti-Markovnikov and Markovnikov rules, also from hydride addition toward double bond of cyclic fragment in the mixture of exo- and endo-forms, is not available, because of the complicated character of the spectra.

We have carried out wide-angle X-ray analyses for synthesized oligomers. Figure 6 shows that the oligomer II is one-phase amorphous system. Diffraction patterns display two maxima. The main one at $2\theta = 9.5^\circ$ corresponds to interchain distance $d_1 = 9.31 \text{ \AA}$, whereas the second one at $2\theta = 16.5^\circ$ corresponds to $d_2 = 5.37 \text{ \AA}$, which characterizes both

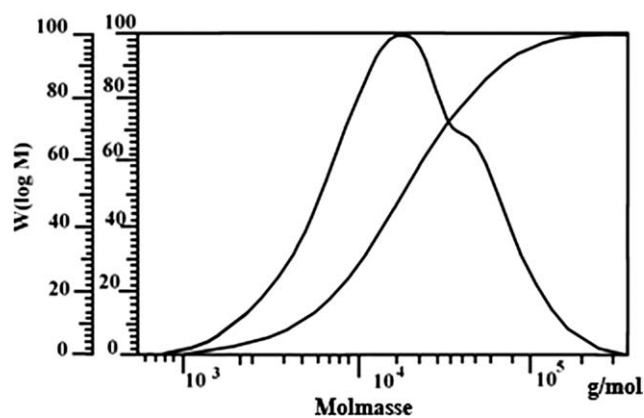


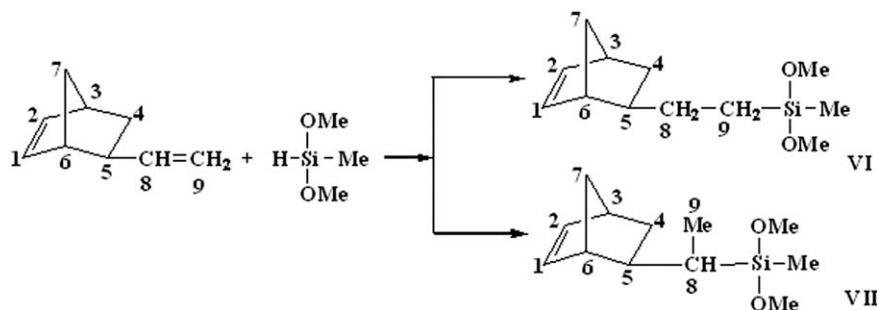
Figure 7 Gel permeation chromatographic curves of oligomer II.

intramolecular and interchain interactions.¹⁹ The change of reaction conditions or used catalyst does not influence on value of interchain distances.

For synthesized oligomer II, gel permeation chromatographic investigation was studied. Figure 7 shows the molecular weight distribution of oligomer II. Oligomer has bimodal molecular weight distribution. For some oligomers, the average molecular weights were determined: $M_n \approx 7.70 \times 10^3$, $M_w = 2.97 \times 10^4$, and polydispersity is equal to $D = 3.8$.

The average number molecular weight of oligomer II exceeds 4.6 times the theoretical value calculated for the full hydrosilylation, which is equal to 6462. This shows that during intermolecular hydrosilylation reaction partially the branching processes also takes place.

Synthesized oligomers were investigated by DSC analyses. For oligomer I, there is only single endothermic peak, which corresponds to the glass transition temperature and is equal to $T_g \approx -54^\circ\text{C}$. 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),²² and 4-vinyl-1-cyclohexene (-57°C).²³



Scheme 6 Modeling hydrosilylation reaction of $[\text{Me}(\text{MeO})_2\text{SiH}]$ with 5-vinyl-2-norbornene according to the anti-Markovnikov and Markovnikov rule.

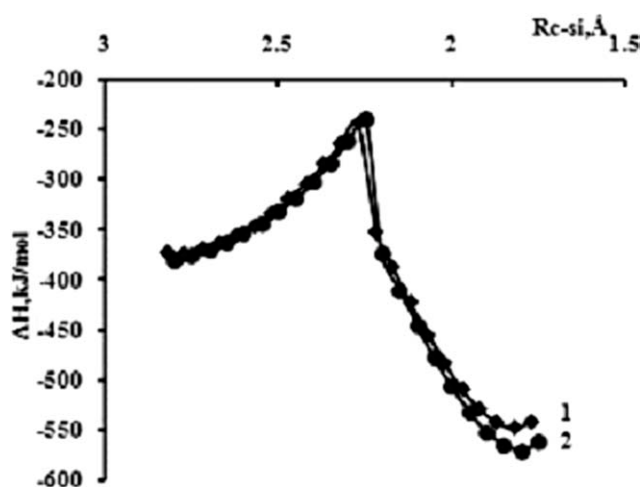


Figure 8 The change of energy (ΔH) as a function of the distance R_{C-Si} between silicon and carbon atoms from modeling hydrosilylation reaction of methyl-dimethoxy-silane with 5-vinyl-2-norbornene according to the Markovnikov (1) and anti-Markovnikov (2) rule.

It must be noted that additionally oligomer II was heated for 2–3 h at 50–60°C temperature, and at this time, the intermolecular hydrosilylation reaction 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.

QUANTUM-CHEMICAL CALCULATIONS

Semi-empirical quantum methods are simplified versions of the Hartree-Fock approach using empirical corrections derived from experimental data. These methods are usually referred using acronyms encoding some of the underlying theoretical assumptions. We apply one of the most frequently used AM1 methods. It is based on the neglect of differential diatomic overlap (NDDO) integral approximation. This approach belongs to the class of zero differential overlap (ZDO) methods, in which all two-electron integrals involving two-center charge distributions are neglected. A number of additional approximations are made to speed up calculations and a number of parameterized corrections are made to correct for the approximate quantum me-

chanical model. For AM1, the parameterization is performed so that we obtain enthalpies of formation H^{form} instead of total enthalpies²⁴ as a function of the distance R_{C-Si} . The calculations provide us also with P_{x-y} values, which represent bond orders.

The purpose of these calculations is the development of the method for the prediction of hydrosilylation reactions' directions. This method chemists can use as an aid to experiment, in particular in studies of reaction mechanisms. A major problem in studying reactions by any current theoretical model is the lack of experimental data; because of this we have performed calculations parallel with experiment.

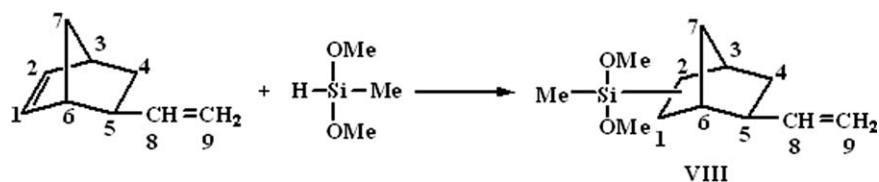
We have performed calculations using a semi-empirical AM1 method for modeling reaction between methyl-dimethoxy-silane [Me(MeO)₂SiH] and 5-vinyl-2-norbornene for full characterization of hydride addition of polymethylhydrosiloxane to 5-vinyl-2-norbornene using software Chem3D Ultra 9.0 from Cambridge Soft.

Using quantum-chemical half empiric AM1 method, we have calculated the heats of formations (ΔH_f), changes of system energy (ΔH) depending on the change of distance (R_{C-Si}) between $\equiv C-Si$ bonds, also the charge values (q) on the atoms, dipole moments (μ), and bonds orders (P_{ij}) for all: initial, intermediate, and final products, in modeling reaction of hydrosilylation of methyl-dimethoxy-silane with 5-vinyl-2-norbornene.

We have discussed the hydrosilylation reaction of model compound—methyl-dimethoxy-silane with 5-vinyl-2-norbornene according to the anti-Markovnikov and Markovnikov rules with substituted vinyl group and also hydride addition toward double bond of the bicyclic fragment.

First, we have considered the modeling hydride addition reaction of [Me(MeO)₂SiH] with 5-vinyl-2-norbornene according to the anti-Markovnikov and Markovnikov rule. The model reaction proceeds according to the following Scheme 6 by obtaining compounds VI and VII, respectively.

The distance between the double bonded C₈ and C₉ carbon atoms and silicon atom was assumed 1.0 Å longer than the bond length as expected in the product. The change of the distance R_{C-Si} between the atom of silicon and the double bonded carbon atom was 0.05 Å. The change of energy (ΔH)



Scheme 7 Modeling hydrosilylation reaction of [Me(MeO)₂SiH] with 5-vinyl-2-norbornene toward $-CH=CH-$ double bond.

calculated from AM1 as a function of the distance R_{C-Si} is presented in Figure 8 (curves 1 and 2).

We have also considered the modeling hydrosilylation reaction of methyldimethoxysilane [$Me(MeO)_2SiH$] with 5-vinyl-2-norbornene between the $-CH=CH-$ double bonded C_1 and C_2 carbon atoms in bicyclic fragment. The model reaction proceeds according to the following Scheme 7 with formation of compound VIII.

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 9.

Using quantum-chemical half empiric AM1 method, we have calculated activation energies E_{act} and the heats of formation (ΔH) of the hydrosilylation reactions and their products. It was found that the value of activation energy and heats of formation toward of double bonded C_1 and C_2 carbon atoms is approximately the same (see Table II). From Figures 8 and 9, it is obvious that ΔH monotonously decreases with decreasing distance, whereas strengthening of recently formed bonds occurs. Activation energies for the modeling reactions were calculated from the difference of the maxima and the initial points from Figures 8 and 9, respectively. The activation energies and heats of formations for all three directions are given in the following table.

Taking into account activation energies and heats of formations, we can conclude that reaction can proceed according to all three directions: anti-Markovnikov addition, Markovnikov addition, and addition with double bond of norbornene fragment. The results of calculations are close to each other and it

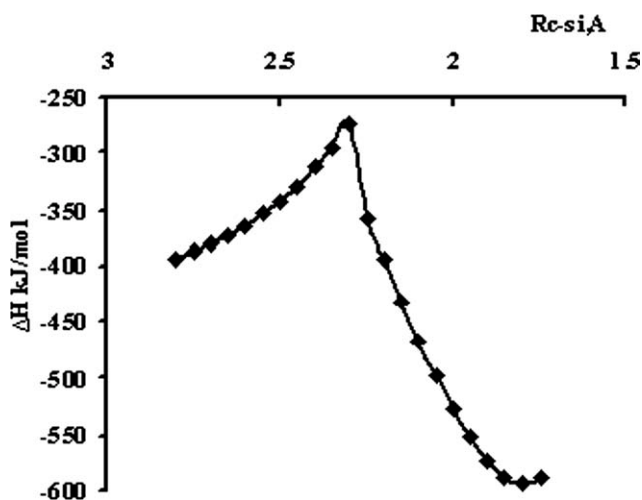


Figure 9 The change of energy (ΔH) as a function of the distance R_{C-Si} between silicon and carbon atoms from modeling hydrosilylation reaction of methyldimethoxysilane with 5-vinyl-2-norbornene toward double bond in the bicyclic fragment.

TABLE II
Heats of Formations and Activation Energies for Modeling Hydrosilylation Reaction of Methyldimethoxysilane with 5-Vinyl-2-norbornene

Reaction direction	Heat of formation, ΔH (kJ mol ⁻¹)	Activation energy, E_{act} (kJ mol ⁻¹)
Anti-Markovnikov rule	-188.64	142.71
Markovnikov rule	-173.104	130.84
Hydrosilylation toward the double bond of bicyclic fragment	-200.03	120.39

is difficult to conclude, which direction is energetically most favorable. The results of theoretical calculations are in good agreement with NMR spectral data, which show proceeding of all three directions. Thus, this method proves validity of the method for prediction of hydrosilylation reaction direction as a rough approximation.

CONCLUSIONS

Hydrosilylation reaction of α,ω -bis(trimethylsiloxy)-methylhydrosiloxane with 5-vinyl-2-norbornene in the presence of a catalyst was performed at various temperatures and thermoreactive methylsiloxane oligomers with unsaturated side groups in the side chains have been obtained. It was shown that the hydrosilylation reaction proceeds according to anti-Markovnikov rule, Markovnikov rule, and with double bond of bicyclic fragment. Synthesized oligomers were successfully used for preparation of siliconorganic rubbers, which are still under investigations and will be reported in a separate publication.

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