

Hydrosilylation Reactions of Methylhydridesiloxane to Styrene and α -Methylstyrene

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ABSTRACT: The hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydridesiloxane to styrene and α -methylstyrene in the presence of the catalyst platinum hydrochloric acid (a 0.1M solution in tetrahydrofuran) at a 1:35 ratio of initial compounds at various temperatures (80–90°C) was investigated, and methylsiloxane oligomers with aryl-substituted groups in the side chain were obtained. Complete hydrosilylation of all active $\equiv\text{Si}-\text{H}$ groups did not take place. The hydrosilylation reaction order, activation energies, and rate constants were determined. The synthesized oligomers were characterized by ^1H , ^{13}C , and IR spectral data. For the full characterization of the hydride addition of methylhydridesiloxane to styrene by the quantum-chemical half-empiric Austin Model 1 (AM1) method for all initial,

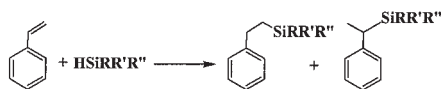
intermediate, and final products, in the modeling of the hydrosilylation reaction of methyltrimethoxysilane to styrene, the heats of formation, energy changes of the system depending on the change of distance between $\equiv\text{C}-\text{Si}\equiv$ bonds, and the charge values on the atoms, dipole moments, and bond orders were calculated. The synthesized oligomers were characterized by gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis, and wide-angle X-ray diffraction. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 388–394, 2006

Key words: polymethylhydridesiloxane; hydrosilylation; thermal properties

INTRODUCTION

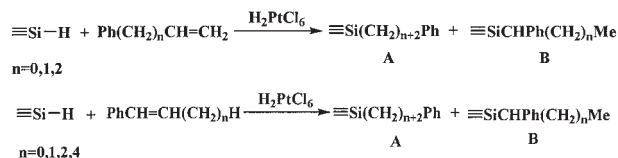
In the literature, there are known hydride addition reactions of organohydridechloro(fluor)silanes with styrene in the presence of a Speier catalyst^{1–3} and Pt/C (on the carbon-adsorbed platinum).^{4–6} There are varying opinions about the direction of hydride addition reactions of organohydridechlorosilanes with styrene, including that the reaction proceeds according to the Farmer rule or according to the Markovnikov rule. The steric and inductive effects of the displaced groups considerably influence the reaction direction.

In the literature, it has been shown that styrene is especially active in hydrosilylation reactions, processes that frequently proceed at room temperature; as catalysts, compounds of Pt, Pd, Rh, and Ni are often used. Depending on the type of the silanes used, the addition of hydrosilanes can occur both α , and β to the double-bonded carbon.^{7,8}



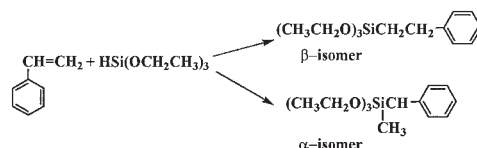
where $\text{R} = \text{R}' = \text{R}''$ and $\text{R} \neq \text{R}' \neq \text{R}''$.

Musolf and Speier⁹ investigated the interaction of phenyl alkenes with the general formula $\text{Ph}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ or $\text{PhCH}=\text{CH}(\text{CH}_2)_n\text{H}$ (where $n = 0-4$) with various hydrosilanes in the presence of H_2PtCl_6 :



In both cases, the reaction proceeded with the formation of two products: A and B. The quantity ratio of these products depended on the nature of the olefins and groups attached to silicon in the hydrosilanes.

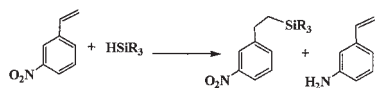
The hydrosilylation reaction of triethoxysilane to styrene in the presence of Karstedt's catalyst has also been investigated.¹⁰ It was established that the reaction proceeded according to two directions with the formation α and β isomers. The ratio between products was about 39:61:



Chernishev et al.¹¹ investigated the reaction abilities of fluoroarylsilanes. They established that fluoroaryl-

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silanes formed both products of hydrosilylation, basically α isomers, and in the case of fluorodiphenylsilanes, identical quantities of α and β isomers were formed. During these processes, the field effect and steric effects played significant roles. Fluorohydrosilanes, in comparison with chloroderivatives, have a higher reactivity.¹¹ In case of *m*-nitrostyrene, it can be reduced to aminostyrene. The replacement of alkyl-substituted groups by aryl groups causes the slowing of the process rate, and the reaction basically proceeds in the direction of reduction. In the case of the addition of triphenylsilane, the reaction proceeds completely in the reduction direction:¹²



Significant studies were carried out by Reikhsfield and Astrakhanov.^{13,14} They investigated the kinetic regularity of the hydrosilylation of different hydrosilanes to arylalkenes ($\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$) in the presence of platinum complexes.

Researchers^{15,16} have carried out the hydrosilylations of chlorophenyl, phenyldicyclohexyl, butyl, and isoamilsilane to α -methylstyrene in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (a 0.1M solution in tetrahydrofuran). In all cases, addition occurred to the final carbon atom, and monoaddition products were predominantly obtained. The kinetic investigation of the hydrosilylation reaction of phenylsilane and isoamilsilane with α -methylstyrene at various temperatures in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (a 0.1M solution in tetrahydrofuran) was carried out. It was concluded that the reaction proceeded faster when the positive charges on the silicon atom and the electronic density of the double bond were greater.

EXPERIMENTAL

The starting materials for the synthesis of methylarylsiloxane oligomers were α,ω -bis(trimethylsiloxy)methylhydridesiloxane styrene and α -methylstyrene.

The initial α,ω -bis(trimethylsiloxy)methylhydridesiloxane with a degree of polymerization of approximately 35, styrene, and α -methylstyrene were received from Fluka. The organic solvents were cleaned by drying and distillation.

IR spectra of all samples were taken on an UR-20 instrument (Zeiss) from KBr pellets, whereas the ^1H and ^{13}C -NMR spectra were taken on a Perkin-Elmer R34 spectrometer instrument at an operating frequency of 250 MHz. All spectra were obtained with the use of CDCl_3 as the solvent and internal standard. A Perkin-Elmer DSC-2 differential scanning calorimeter was used for thermogravimetric analysis, and the thermal transitions [glass-transition temperatures

(T_g 's)] were read at the maximum endothermic or exothermic peaks. Heating and cooling scanning rates were $10^\circ\text{C}/\text{min}$.

Gel permeation chromatography investigation was carried out with the use of a Waters model 6000A chromatograph with an R 401 differential refractometer detector (Milford, MA, USA). The column set comprised 10^3 and 10^4 Å Ultrastaygel columns. The sample concentration was approximately 3 wt % in toluene, and the typical injection volume for the siloxanes was 5 μL . Standardization of the gel permeation chromatograph was accomplished with the use of styrene or polydimethylsiloxane (PDMS) standards with the known molecular weight.

Wide-angle X-ray diffractograms were taken on a DRON-2 instrument (Burevestnik, Saint Petersburg, Russia). Cu K α was measured without a filter, the angular velocity of the motor was approximately $2^\circ/\text{min}$.

Hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydridesiloxane to styrene

The hydrosilylation reaction was carried out in a three-necked flask equipped with a tube for a catalyst inlet, reflux condenser, inert gas carrier tube, and mechanical stirrer.

The reaction products [0.9768 g (0.49 mmol) α,ω -bis(trimethylsiloxy)methylhydridesiloxane and 1.5533 g (0.0149 mol) styrene] and 5.4 mL of dry toluene were placed into the flask and thermostated in an oil bath until a constant temperature of 90°C was reached. Then, the catalyst [a 0.1M solution of platinum hydrochloric acid in tetrahydrofuran ($5-9 \times 10^{-5}$ g/1.0 g of starting substance)] was introduced. The percentage of active $\equiv\text{Si}-\text{H}$ was determined by the Chugaev-Cerretinov method during the reaction. After the reaction finished, the solvent was partially eliminated, the reaction product was precipitated from a toluene solution by *n*-hexane, and 2.36 g (91%) of oligomer I¹ was obtained. The hydrosilylation reaction with α -methylstyrene and styrene at various temperatures (80 and 85°C) was carried out by the aforementioned method.

RESULTS AND DISCUSSION

From literature, it is known that the insertion of various heteroatoms or cyclic fragments in the linear dimethylsiloxane backbone breaks the spiral structure of the PDMS chain and changes the physicochemical indices and thermooxidative stability of the copolymers.¹⁷ The insertion of more rigid phenyl fragments in the main PDMS backbone hinders the depolymerization processes of the polymeric chain, which is accompanied by a release of cyclic D_n -type dimethyl-

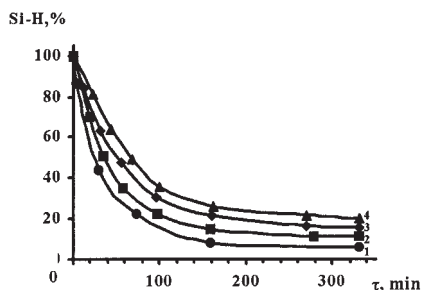


Figure 1 Dependence of the changes in concentration of active $\equiv\text{Si}-\text{H}$ groups on time in the hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydridesiloxane to styrene and α -methylstyrene, where curves 1, 2, and 4 correspond to the hydride addition of methylhydridesiloxane to styrene at 90, 85, and 80°C, respectively, and curve 3 corresponds to the hydride addition of methylhydridesiloxane to α -methylstyrene at 90°C.

cyclosiloxanes ($[\text{Me}_2\text{SiO}]_n$'s). Such polymers are characterized by higher thermooxidative stabilities. The increased thermooxidative stability of the copolymers may be explained by the presence of phenyl groups with high resistances to oxidation and with inhibiting effects on the oxidation of methyl groups.^{18,19}

The aim of our study was, by means of the modification reaction of methylhydridesiloxane, the synthesis of new organosilicone oligomers with various aryl groups in a side chain. As starting materials, α,ω -trimethylsilyloxymethylhydridesiloxane, styrene, and α -methylstyrene were used.

For the purpose of the synthesis of linear organosilicone monomers with aryl side groups, the hydrosilylation reaction of α,ω -trimethylsilyloxymethylhydridesiloxane (degree of polymerization ≈ 35) to styrene and α -methylstyrene were studied.

Through the preliminary heating of the initial compounds in the temperature range 80–90°C in the presence of the catalyst, we established that in these conditions, polymerization, the elimination of hydrogen, and other changes in the initial compounds did not take place.

Hydrosilylation reactions at a 1:35 molar ratio in the presence of platinum hydrochloric acid as a catalyst at various temperatures (80, 85, and 90°C) in an absolutely dry toluene solution (C (concentration of solution) = 0.15 mol/L) were studied. The course of the reaction was observed by the decreasing amount of active $\equiv\text{Si}-\text{H}$ groups.

We established that during the hydrosilylation reaction, all active $\equiv\text{Si}-\text{H}$ groups did not react. Figure 1 shows the dependence of the changes in concentration of the active $\equiv\text{Si}-\text{H}$ group on time in the hydrosilylation reactions of α,ω -bis(trimethylsiloxy)methylhydridesiloxane to styrene (80, 85, and 90°C) and α -methylstyrene (90°C).

As shown in Figure 1, with increasing temperature during the hydrosilylation of methylhydridesiloxane

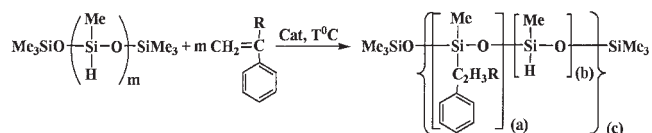
to styrene, the conversion of active $\equiv\text{Si}-\text{H}$ groups increased from 77% (curve 4) to 95% (curve 1). In case of α -methylstyrene, the conversion of active $\equiv\text{Si}-\text{H}$ groups at 90°C was 80%. The low depth of the hydrosilylation reaction may have been due to steric effects evoked by methyl groups in α -methylstyrene.

The hydrosilylation reactions of α,ω -bis(trimethylsiloxy)methylhydridesiloxane to styrene and α -methylstyrene generally proceeded according to Scheme 1, in which $[(a) + (b)](c) = m \approx 35$; $\text{R}=\text{H}$ ($\text{I}^1 = 80^\circ\text{C}$; $\text{I}^2 = 85^\circ\text{C}$; $\text{I} = 90^\circ\text{C}$); Me ($\text{II} = 90^\circ\text{C}$).

The hydrosilylation reaction mainly proceeded rapidly in the first hours, and then, the reaction proceeded at a low rate. Transparent oligomers with $\eta_{\text{sp}} \approx 0.07\text{--}0.09$ that were well soluble in aromatic types of organic solvents were obtained. By functional and elementary analysis and by IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectral data, the composition and structure of the obtained oligomers were established. Some physicochemical properties and yields of synthesized oligomers are presented in Table I.

In the IR spectra of the synthesized oligomers at 2160–2165 cm^{-1} , we observed absorption bands characteristic for unreacted $\equiv\text{Si}-\text{H}$ bonds. This indicated that during hydrosilylation, the conversion of all active $\equiv\text{Si}-\text{H}$ groups did not take place. In the IR spectra of the oligomers, we observed characteristic bands for the asymmetric valence oscillation of the linear $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds at 1020 cm^{-1} and characteristic bands for $\equiv\text{Si}-\text{Me}$ and $-\text{SiMe}_3$ bonds at 1275 and 840 cm^{-1} , respectively. In the spectra, we observed characteristic bands for monosubstituted benzene rings in the ranges 720, 1490–1600, and 3030–3070 cm^{-1} . Absorption bands at 1130 and 1435 cm^{-1} indicated the presence of phenyl groups.

In the $^1\text{H-NMR}$ spectra of oligomer I (Fig. 2), we observed a singlet signal of protons in the methyl groups in the $\equiv\text{Si}-\text{Me}$, $-\text{SiMe}_3$ fragment with a chemical shift of $\delta = 0.1$ and $\delta = 0.3$ ppm, and a broadened signal of protons in the $-\text{CH}-\text{CH}_3$ fragment with a chemical shift of $\delta = 0.8$ ppm. Also, we observed a broadened signal of methylene protons in the $\equiv\text{Si}-\text{CH}_2-$ fragment with a chemical shift of $\delta = 1.2$ ppm, which indicated that the hydride addition reaction also proceeded according to the Markovnikov rule. In the $^1\text{H-NMR}$ spectra, we also observed a low-intensity signal with the center of the chemical shift at



Scheme 1 Hydrosilylation reactions of α,ω -bis(trimethylsiloxy)methylhydridesiloxane to styrene and α -methylstyrene.

TABLE I
Some Physicochemical Properties and Yields of Synthesized Oligomers

| Oligomer | Reaction temperature (°C) | Yield (%) | η_{sp}^a | $M_w \times 10^{-3}$, $M_n \times 10^{-3}$, and D | T_g (°C) | d_1 (Å) ^b | 5% mass losses |
|----------------|---------------------------|-----------|---------------|--|------------|------------------------|----------------|
| I ¹ | 80 | 91 | 0.07 | — | -65 | — | — |
| I ² | 85 | 92 | 0.07 | — | — | — | — |
| I | 90 | 94 | 0.09 | 15.94 5.10 3.03 | -50 | 8.52 | 280 |
| II | 90 | 91 | 0.07 | 34.21 9.75 3.51 | -56 | 8.48 | 275 |

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

^b d_1 is inter-chain distance.

$\delta = 4.3$ ppm, which characterized the unreacted $\equiv\text{Si}-\text{H}$ bonds. The results of the $^1\text{H-NMR}$ spectra together with the IR spectral data indicated the various linked structures of the synthesized oligomers.

In the $^1\text{H-NMR}$ spectra, we also observed a broadened signal in a low field with the center of chemical shift at $\delta = 2.6$ ppm, which was characteristic for protons in the methylene group in the $\text{Ph}-\text{CH}_2$ fragment. In the spectra, we observed a multiplet signal characteristic of protons of the phenyl group in the range $\delta = 6.7-7.4$ ppm. The ratio of isomers obtained according to the Farmer and Markovnikov rules was about 1.2:1.

In the $^{13}\text{C-NMR}$ spectra of oligomer I (Fig. 3), we observed a signal with a chemical shift at $\delta = 21.9$ ppm, which was characteristic of the carbon of the methylene group attached with silicon ($\equiv\text{Si}-\text{CH}_2-$); a signal with a chemical shift at $\delta = 30.9$ ppm, which was characteristic of the carbon of the methylene group in the $\text{Ph}-\text{CH}_2$ fragment; a signal at $\delta = 29.4$ ppm, which was characteristic for methine (CH) groups in the $\text{CH}-\text{CH}_3$ fragment; and a signal at $\delta = 15.2$ ppm, which was referred to as the carbon of the methyl group in the $\text{CH}-\text{CH}_3$ fragment.

The $^1\text{H-NMR}$ spectra of oligomer II (Fig. 4) contained singlet signals of the protons of the methyl group in the $\equiv\text{Si}-\text{Me}$, $-\text{SiMe}_3$ fragments with chem-

ical shifts of $\delta = 0.1$ and 0.3 ppm and a broadened signal of the protons of the methylene group in the $\equiv\text{C}-\text{CH}_3$ fragment, with a chemical shift of $\delta = 1.0$ ppm. In this spectrum, we also observed a broadened signal of methyl protons in the $-\text{Si}-\text{CH}_2-$ fragment with a chemical shift of $\delta = 1.3$ ppm.

We also observed a wide signal of methyl protons in the $=\text{CH}-\text{CH}_3$ fragment with a chemical shift of $\delta = 1.3$ ppm and a broadened signal with a center of $\delta = 3.0$ ppm, which was characteristic for protons of the CH group in the same fragment. The results of the $^1\text{H-NMR}$ spectra indicate that the hydride addition reaction proceeded according to the Farmer and Markovnikov rules.

The $^{13}\text{C-NMR}$ spectra of oligomer II (Fig. 5) was in complete agreement with $^1\text{H-NMR}$ spectral data. In the spectra, we saw a resonance signal for the carbon nucleus of the methylene group ($\equiv\text{Si}-\text{CH}_2-$) at the silicon atom with the center of the chemical shift at $\delta = 34.5$ ppm; a resonance signal with the center of the chemical shift at $\delta = 26.8$ ppm, which was characteristic for the carbon nucleus of methine groups in the $\text{Ph}-\text{CH}$ fragment; a signal with the center at $\delta = 25.1$ ppm, which was characteristic for the methyl groups

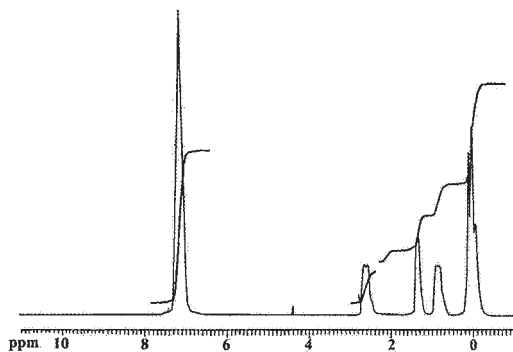


Figure 2 $^1\text{H-NMR}$ spectrum of oligomer I.

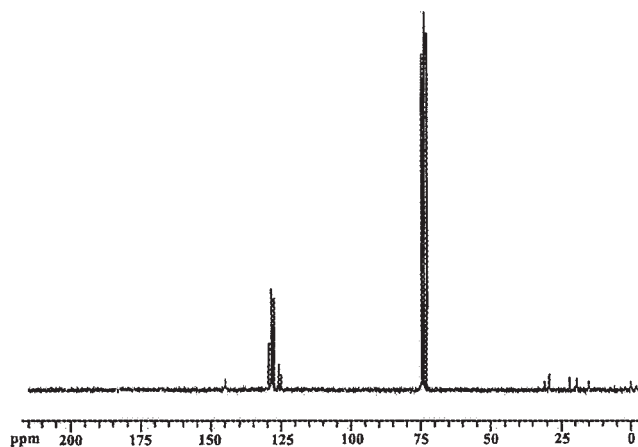


Figure 3 $^{13}\text{C-NMR}$ spectrum of oligomer I.

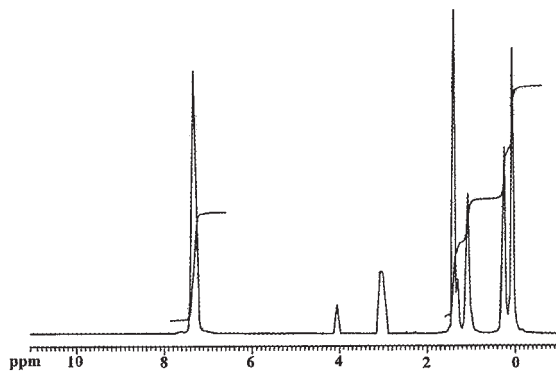


Figure 4 $^1\text{H-NMR}$ spectrum of oligomer II.

in the CH-CH_3 fragment; and a signal at $\delta = 19.6$ ppm, which was characteristic for the carbon nucleus of the methyl group in the $=\text{C}(\text{CH}_3)_2$ fragment. This indicated that the hydride addition of methylhydride-siloxane to α -methylstyrene proceeded by both the Farmer and Markovnikov rules.

For the full characterization of the hydride addition of methylhydridesiloxane to styrene by the quantum-chemical semiempirical AM1 method²⁰ in modeling reaction of the hydrosilylation of methyltrimethoxysilane to styrene, for all of the initial, intermediate, and final products, we calculated the heats of formation (ΔH_f 's), energy changes (ΔH 's) of the system depending on the change of distance (R) between $\equiv\text{C-Si}\equiv$ bonds ($R_{\text{C-Si}}$), and the charge values on the atoms, dipole moments, and bond orders (P_{ij}). The catalyst and solvent effects were not provided for the calculations.

First, we considered the hydride addition of the modeling compound methyltrimethoxysilane [$\text{Me}(\text{MeO})_2\text{SiH}$] to styrene according to the Farmer rule. The reaction of the hydride addition by the Farmer rule proceeded according to Scheme 2 with the formation of compound III.

In styrene, $R_{\text{C}_8-\text{Si}}$ was taken as about 1.0 \AA more than the bond length, as expected in the product.

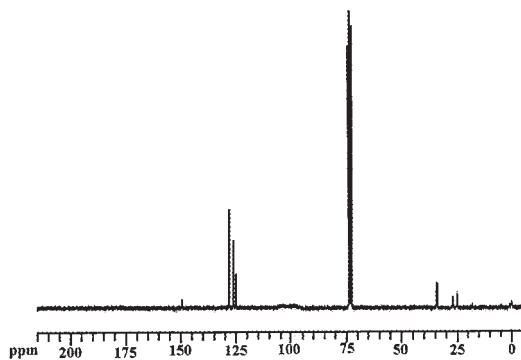
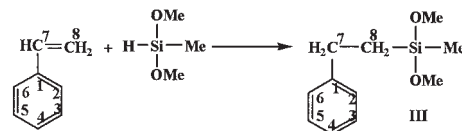


Figure 5 $^{13}\text{C-NMR}$ spectrum of oligomer II.



Scheme 2 Modeling reaction of the hydride addition of methyltrimethoxysilane to styrene according to the Farmer rule.

The change step of $R_{\text{C-Si}}$ between silicon and the double-bonded carbon atom C_8 was about 0.05 \AA . The dependence of ΔH of the system on $R_{\text{C-Si}}$ is presented in Figure 6.

As shown in Figure 6, at approximations of silicon to carbon C_8 up to $R_{\text{C-Si}} = 2.25 \text{ \AA}$, the system energy rose. At the same time, P_{ij} between carbons C_8 and C_7 in the styrene molecule decreased from 1.922 to 1.640. $P_{\text{H-Si}}$ also decreased ($R_{\text{Si-H}} = 0.888-0.693$), and for the modeling compound methyltrimethoxysilane, the formation of new bonds ($P_{\text{C-Si}} = 0.017-0.127$ and $P_{\text{C-H}} = 0.002-0.099$) was observed. For R values up to 2.20 \AA , the system energy sharply decreased, the C=C bond passed in an ordinary C-C bond ($P_{\text{C-C}} = 1.004$), and $P_{\text{C}_8-\text{Si}}$ reached 0.861. Thus, the hydrogen was completely eliminated from silicon ($P_{\text{Si-H}} = 0.011$) and attached to carbon atom C_7 ($P_{\text{C-H}} = 0.918$).

With the consecutive reduction of distances, the system energy monotonously decreased and, with strengthening, formed new bonds. ΔH_f of the hydrosilylation product ($\Delta H_f = -595.4 \text{ kJ/mol}$) had a good correlation with the ΔH_f ($\Delta H = -601.2 \text{ kJ/mol}$) of compound III obtained by the hydride addition of methyltrimethoxysilane to styrene according to the Farmer rule. The activation energy (E_{act}) of the modeling reaction proceeding by Farmer rule was equal to 89.6 kJ/mol .

The modeling hydrosilylation reaction of methyltrimethoxysilane to styrene according to the Markovnikov rule was also considered. The modeling reaction proceeded according to Scheme 3 with the formation of compound IV.

In Figure 7, the dependence of ΔH of the system on $R_{\text{C}_7-\text{Si}}$ is presented. Similarly, the aforementioned $R_{\text{C}_7-\text{Si}}$ was taken as about 1.0 \AA more than the bond, as

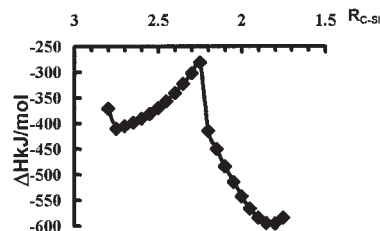


Figure 6 Dependence of ΔH on $R_{\text{C}_8-\text{Si}}$ during the modeling of the hydride addition reaction of methyltrimethoxysilane to styrene according to the Farmer rule.

expected in a product. The change step of R_{C-Si} between the silicon atom and double-bonded carbon C_7 was about 0.05 Å

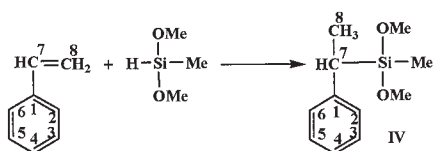
As shown in Figure 7, at approximations of silicon to carbon C_7 up to $R_{C-Si} = 2.00$ Å, the system energy rose. At the same time, $P_{C_7-C_8}$ in the styrene molecule decreased from 1.894 to 1.556. P_{H-Si} also decreased ($R_{Si-H} = 0.877-0.669$), and in methyltrimethoxysilane, the formation of new bonds ($P_{C-Si} = 0.016-0.197$ and $P_{C-H} = 0.011-0.065$) was observed. For R values up to 1.95 Å, the system energy sharply decreased, the double $C=C$ passed in ordinary $C-C$ bond ($P_{C-C} = 1.006$), and P_{Si-C_7} reached 0.794. Thus, the hydrogen was completely eliminated from silicon ($P_{Si-H} = 0.019$) and attached to carbon C_8 ($P_{C-H} = 0.932$).

With the consecutive reduction of distances, the system energy monotonously decreased and, with strengthening, formed new bonds. ΔH_f of the product of hydride addition ($\Delta H_f = -448.4$ kJ/mol) had a good correlation with ΔH_f ($\Delta H = -454.2$ kJ/mol) of compound **IV** obtained by the hydride addition of methyltrimethoxysilane to styrene according to the Markovnikov rule. E_{act} of the modeling reaction proceeding by the Markovnikov rule was equal to 156.4 kJ/mol.

Thus, with the comparison of the ΔH_f values of compounds **III** and **IV**, E_{act} 's, and also of Figures 6 and 7 (the character of the curves of ΔH and the P_{ij} values), we concluded that the course of modeling the hydrosilylation reaction of methyltrimethoxysilane to styrene energetically was more favorable by the Farmer rule, which was in agreement with the NMR spectral data, but the difference was closely approximated (Farmer rule:Markovnikov rule = 1.2:1).

In Figure 8, the dependence of the reverse concentration on the time of the hydrosilylation reaction of methylhydridesiloxane to styrene is presented. The hydrosilylation reaction at the initial stages was second order. The hydrosilylation reaction rate orders (k 's) at various temperature were calculated as $k_{90^\circ C} \approx 3.0797 \times 10^{-2}$, $k_{85^\circ C} \approx 2.3007 \times 10^{-2}$, and $k_{80^\circ C} \approx 1.6781 \times 10^{-2}$ 1/mol/l s.

From the dependence of the reverse temperature on the logarithm of the rate constants, E_{act} of the hydrosilylation reaction was found to be approximately 66.7 kJ/mol.



Scheme 3 Modeling reaction of the hydride addition of methyltrimethoxysilane to styrene according to the Markovnikov rule.

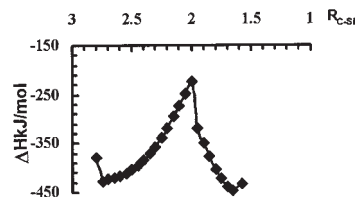


Figure 7 Dependence of ΔH on R_{C_7-Si} during the modeling of the hydride addition reaction of methyltrimethoxysilane to styrene according to the Markovnikov rule.

The synthesized oligomers were studied by gel permeation chromatography. Oligomers **I** and **II** had bimodal molecular weight distributions. For the synthesized oligomers, the average molecular masses were determined. For oligomer **I**, the weight-average molecular weight (M_w) was approximately 1.59×10^4 , the number-average molecular weight (M_n) was approximately 5.17×10^3 , the z -average molecular weight (M_z) was approximately 2.913×10^4 , and the polydispersity was 3.08. For oligomer **II**, M_w was approximately 3.42×10^4 , M_n was approximately 9.75×10^3 , M_z was approximately 1.18×10^5 , and the polydispersity was 3.51.

As shown in Table I, the molecular masses we found exceeded the calculated molecular masses by three to six times. The increased molecular masses proved that during the hydrosilylation reaction, branched oligomers were obtained. The production of branching systems may have proceeded with the participation of residual $\equiv Si-H$ groups in intermolecular crosslinking reactions with the production of $\equiv Si-O-Si \equiv$ and $\equiv Si-Si \equiv$ bonds, which was discussed earlier.^{21,22}

With differential scanning calorimetry, we characterized the oligomers with one endothermic peak, which corresponded to T_g . For oligomer **I**, T_g was approximately $-50^\circ C$, and for oligomer **II**, T_g was approximately $-56^\circ C$.

Thermogravimetric investigations of the synthesized oligomers were carried out. For oligomers, mass losses at $250^\circ C$ were not observed, whereas the unblocked PDMS polymer was completely destroyed in the temperature range $270-280^\circ C$.⁷ Mass losses of 5% were observed at about $350^\circ C$; the main destruction process proceeded from $400^\circ C$. The modification effect induced by the insertion of aryl fragments in the dimethylsiloxane chain increased the thermooxidative stability of the synthesized oligomers.

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