

# Hydride Addition of Methylhydridesiloxanes to Conjugated Cyclohexa-1,3-diene

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**ABSTRACT:** The reaction of hydride polyaddition of methylhydridesiloxanes to conjugated cyclohexa-1,3-diene, in the presence of catalytic amount of platinum hydrochloric acid, has been investigated at several temperatures. The polyorganosiloxanes with cyclohexenyl fragments in the side chain, completely soluble in organic solvents, were synthesized. The hydride polyaddition reaction order, activation energies, and rate constants were found. By quantum-chemical half-empirical method AM1, the electronic characteristics of cyclohexa-1,3-diene: the charges on the carbon atoms and bonds orders were calculated. For full characterization of hydrosilylation reaction, calculations for modeling reaction between methyltrimethoxysilane and cyclohexa-1,3-diene were carried out using Gaussian 03 program package. The geometries of

reactants, transition states, and products were optimized using PM3 semiempirical method followed by single-point calculations at B3LYP/6-31G(d) level of density functional theory. It was concluded that the course of hydride addition of modeling reaction of methyltrimethoxysilane to cyclohexa-1,3-diene energetically is more favorable by 1,4-addition. The synthesized oligomers were characterized by FTIR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy, thermogravimetry, gel permeation chromatography, differential scanning calorimetry, and wide-angle X-ray diffractometry. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1131–1137, 2010

**Key words:** polysiloxanes; oligomers; thermogravimetric analyses; NMR; gel permeation chromatography; hydride polyaddition

## INTRODUCTION

The properties of siliconorganic polymers depend as on the structure of a macromolecular chain as well as on the nature of the surrounding organic groups at silicon atom.<sup>1</sup>

The effective methods of synthesis of new type siliconorganic copolymers with complex valuable properties attract a great attention. Particularly, the synthesis of polyorganosiloxanes with unsaturated surrounding groups at silicon atom, for preparation of siliconorganic rubbers<sup>2</sup> and modifiers for carbon-chain polymers<sup>3</sup> is very important.

In the literature, the modification reactions of the linear polymethylvinylsiloxanes with norbornene groups are known.<sup>4</sup> According to literature data, the synthesized polymers are characterized with higher reaction ability for vulcanisation and thermal-oxidative stability. By the catalytic dehydrocondensation reaction of oligomethylhydridesiloxanes with hydroxyorganocyclosiloxanes in the presence of

powder-like potassium hydroxide, the oligomethylsiloxanes with cyclic fragments in the side chain were synthesized.<sup>5</sup> By hydrosilylation reactions of methyl(ethyl)hydridesiloxane with vinylorganocyclosiloxanes in the presence of platinum hydrochloric acid, polyorganosiloxanes with carboorganocyclosiloxane fragments in the side chain were synthesized.<sup>1,6</sup> In both cases, introduction of reactionable cyclic fragments in the side chain leads to the rise of thermal-oxidative stability and glass transition temperature of copolymers.

By polymerization reaction of methyltricyclodecylcyclotri(tetra)siloxanes in the presence of catalysts, methylsiloxane copolymers with unsaturated tricyclodecyl groups in the chain were obtained.<sup>7</sup>

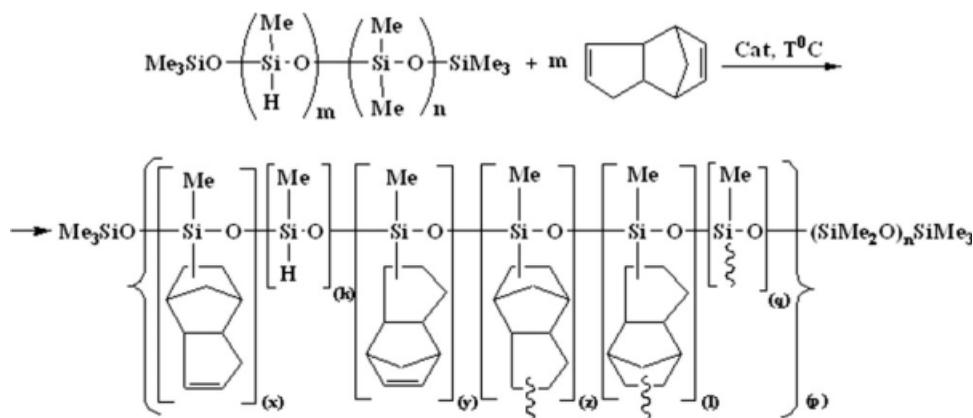
By hydrosilylation reaction of tricyclodecadiene with  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxanes<sup>8</sup> and  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane copolymers<sup>9</sup> in the presence of platinum hydrochloric acid or platinum on the charcoal as catalysts, methylsiloxane oligomers containing various repeating units were synthesized according to the Scheme 1:

where:  $[(x) + (k) + (y) + (z) + (l) + (q)](p) = m \approx 30$ ;  $n = 0, 23$ .

It was established that the rise of temperature causes the rise of yield of three-dimensional (3D) polymers. During hydrosilylation at 90°C, about 20%

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**Scheme 1** Hydrosilylation reaction of tricyclodecadiene with  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane.

insoluble polymers were obtained, this may be explained by the secondary interchain reactions caused by remaining catalyst in reaction system. Soluble oligomers were obtained if conversion of active  $\equiv\text{Si}-\text{H}$  bonds was less than 80%.

## EXPERIMENTAL PART

The starting materials for the synthesis of the linear siloxanes with cyclohexenyl fragments in the side chain were  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxanes with degree of polymerization  $n \approx 30$ , cyclohexa-1,3-diene and catalyst platinum hydrochloric acid. They were obtained from Aldrich and used as received.

The organic solvents were cleaned by drying and distillation. The purity of the starting compounds was controlled by gas-liquid chromatography "LKhM-8-MD" (Russian model), phase SKTF-100 (10%), the NAW chromosorb, carrier gas He, and 2M column.

FTIR spectra were obtained on a Nicolet Nexus 470 machine with MCTB detector.  $^1\text{H-NMR}$  spectra were recorded on an ARX400 Bruker NMR spectrometer at 400 MHz operating frequency, using  $\text{CDCl}_3$  as the solvent and an internal standard.

Gel permeation chromatography (GPC) was carried out by using toluene or THF as an eluent and IR detector. Gel permeation chromatography was carried out using a Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised  $10^3$  and  $10^4$  Å Ultrastragel columns. Sample concentrations were 3% by weight in toluene, and typical injection volume for the siloxane was 5  $\mu\text{L}$ . Standardization of the GPC was accomplished by use of styrene or PDMS standards with the known molecular weight.

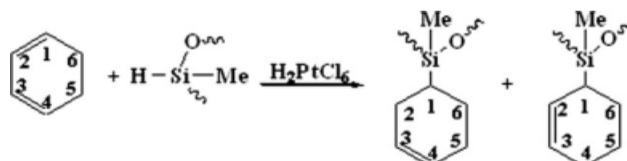
Wide-angle X-ray diffractograms were taken on a "Dron-2" (Burevestnik, Saint-Petersburg, Russia) instrument, using  $\text{A-CuK}_\alpha$  radiation. The values

were measured without a filter, the angular velocity of the motor was  $\omega = 2^\circ/\text{min}$ .

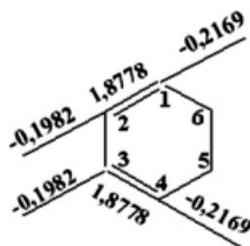
The thermogravimetric investigations were carried out on a "Paulic-Paulic-Erdey" derivatograph model MOM-102 (Hungary). The test conditions: temperature rise rate  $v = 5^\circ/\text{min}$  in the open area.

## Hydrosilylation reaction of $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to cyclohexa-1,3-diene

Hydrosilylation reaction was carried out in a three-necked flask equipped with a tube for catalyst inlet, reflux condenser, and inert gas carrier tube. The initial compounds 1.4699 g (0.7491 mmole)  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane and 1.7978 g (22.473 mmole) cyclohexa-1,3-diene and 5.4 mL dry toluene were placed into the flask and thermostated in an oil bath until constant temperature was set up. Then, the catalyst 0.1M solution of platinum hydrochloric acid in tetrahydrofuran ( $5-9 \times 10^{-5}$  g per 1.0 g of starting substance) was added. The reaction was performed in the argon atmosphere in toluene solution at temperature range  $60-90^\circ\text{C}$ . During reaction, the changes of concentration of active  $\equiv\text{Si}-\text{H}$ % groups in the time was observed. Then, the reaction mixture was precipitated from toluene solution by dry hexane and connected to the vacuum ( $P = 1-2$  mmHg) and dried at  $40-50^\circ\text{C}$  temperature up to constant mass.



**Scheme 2** Possible schemes of hydrosilylation reactions of cyclohexa-1,3-diene.



**Diagram 1** The charge values on the carbon atoms and bond orders in cyclohexa-1,3-diene molecule.

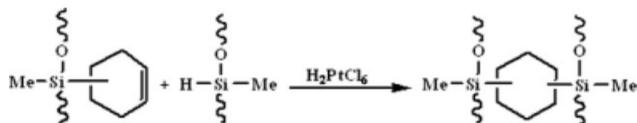
### Computational details

The calculations were performed using Gaussian 03 program package.<sup>10</sup> The geometries of reactants, transition states, and products were optimized using PM3 semiempirical method followed by single-point calculations at B3LYP/6-31G(d) level of density functional theory. In all cases, frequency calculations were performed and the existence of only one imaginary frequency was checked for transition states and no imaginary frequency for minimized reactants and products.

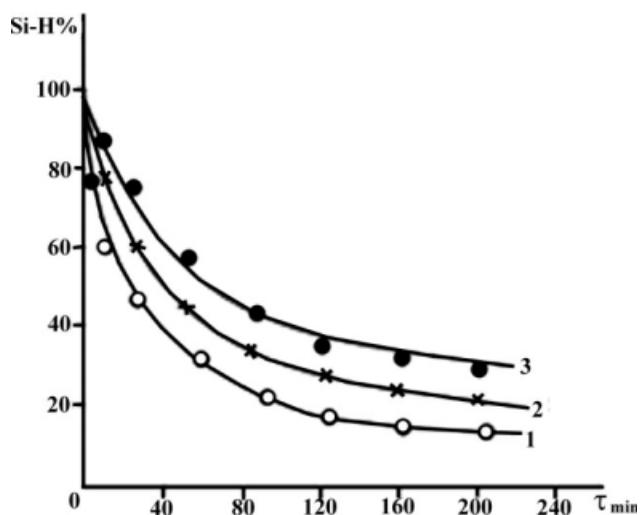
## RESULTS AND DISCUSSION

In the literature, there is no information about linear methylsiloxane polymers containing cyclohexenyl side group. For the purpose of synthesis of the linear siliconorganic elastomers with cyclohexenyl side groups, the modification reactions of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxanes ( $n \approx 30$ ) with cyclohexa-1,3-diene were studied. The hydrosilylation reactions were studied at 1 : 30 molar ratio of initial compounds in the presence of platinum hydrochloric acid as a catalyst. Preliminary heating of initial compounds in the temperature range of 60–90°C in the presence of catalyst showed that in these conditions no changes of initial compounds take place. Besides, there are no changes in the NMR and FTIR spectra of cyclohexa-1,3-diene and methylhydridesiloxanes. By gas-liquid chromatography, it was established that the polymerization of cyclohexa-1,3-diene in this condition does not take place.

As it's seen from the structure of cyclohexa-1,3-diene, the hydrosilylation may proceed with one double bond with preservation of the second one. Besides, hydride addition may be realized either in



**Scheme 3** Possible scheme of intermolecular hydrosilylation.

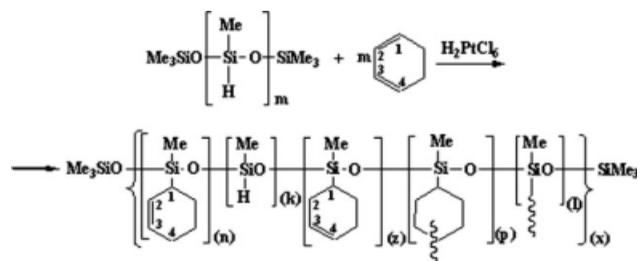


**Figure 1** Dependence of changes of active  $\equiv\text{Si-H}\%$  groups on the time during hydride addition of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxanes to cyclohexa-1,3-diene. Where curve 1 is at 80°C, curve 2 is at 70°C, and curve 3 is at 60°C.

“1–2” direction system in “1–4” direction or as a conjugated diene (Scheme 2):

By quantum-chemical half-empirical method AM1,<sup>11</sup> the electronic characteristics of 1,3-cyclohexadiene: the charges on the carbon atoms and bonds orders were calculated. The obtained results are presented on the molecular Diagram 1.

As it's seen from the molecular diagram, the higher value of the charge is observed on the carbon atoms in 1 and 4 positions. This indicates that these carbon atoms are more reactionable centers for electrophilic addition. Because of that the hydride addition may be realized with more probability in “1–4” position, than 2 or 3 position ( $q_{1,4} \approx -0.2169$ ;  $q_{2,3} \approx -0.1982$ ). The ratio of atom charge values is  $q_{1,4}/q_{2,3} \approx 1.09$ , it is particularly in agreement with NMR spectra data. Besides, bond orders in “1–2” and “3–4” position are characterized with the same values  $P_{1,2} = P_{3,4} \approx 1.8778$ , which indicate that during hydrosilylation decisive role plays the charge values on the atoms.



**Scheme 4** Hydride addition of methylhydridesiloxanes to cyclohexa-1,3-diene.

TABLE I  
Elemental Composition, Yields, and Some Physical–Chemical Properties of Oligomers

| No             | Yield (%) | Reaction temperature (°C) | $\eta_{sp}^*$ | $T_g$ (°C) | $d_1$ (Å) | 5%-Mass losses | $\bar{M}_w \times 10^{-3}$ | Elemental composition, (calc/found) (%) |      |       |
|----------------|-----------|---------------------------|---------------|------------|-----------|----------------|----------------------------|---|------|-------|
|                |           |                           |               |            |           |                |                            | C                                       | H    | Si    |
| I <sup>1</sup> | 94        | 60                        | 0.08          | -14        | 8.40      | 230            | -                          | 59.42                                   | 8.66 | 20.54 |
|                |           |                           |               |            |           |                |                            | 58.95                                   | 8.43 | 21.02 |
| I <sup>2</sup> | 94        | 70                        | 0.08          | -          | -         | -              | -                          | 59.42                                   | 8.66 | 20.54 |
|                |           |                           |               |            |           |                |                            | 59.21                                   | 8.51 | 20.94 |
| I              | 95        | 80                        | 0.09          | -10        | 8.43      | 230            | 48                         | 59.42                                   | 8.66 | 20.54 |
|                |           |                           |               |            |           |                |                            | 59.30                                   | 8.35 | 20.77 |

It was established that during the hydrosilylation reaction in melt condition, at the beginning stages of hydrosilylation (20% of the conversion of active  $\equiv\text{Si-H}$  groups) 3D systems were obtained, which may be explained by intermolecular reactions of macrochain (Scheme 3).

For the purpose of synthesis of soluble organosiloxanes, the hydrosilylation reaction were carried out in absolute dry toluene solution ( $C \approx 0.1155$  mole/L). The course of the reaction was observed by the decrease of the amount of active  $\equiv\text{Si-H}$  groups. As it's seen from Figure 1, with the rise of temperature, the depth of hydrosilylation (conversion of  $\equiv\text{Si-H}$  groups) reaction increases.

After 3 h hydrosilylation reaction at 60°C temperature, the conversion of active  $\equiv\text{Si-H}$  bonds is about 69% (Fig. 1, curve 3). With the rise of the temperature, the conversion of active  $\equiv\text{Si-H}$  bonds increases and at 80°C temperature is about 85% (curve 1). It must be noted that at higher stages of hydrosilylation also 3D systems were obtained. To avoid formation of 3D systems, reaction was stopped at  $\sim 80\%$  depth of  $\equiv\text{Si-H}$  conversion; nevertheless, the intermolecular reactions partially still take place. Overall hydrosilylation reaction of methylhydridesiloxanes to cyclohexa-1,3-diene proceeds according to the following Scheme 4:

where:  $[(n) + (k) + (z) + (p) + (l)](x) = m \approx 30$ , I<sup>1</sup> (60°C); I<sup>2</sup> (70°C); I (80°C).

The synthesized oligomers are vitreous, rubber-like products, well soluble in aromatic type ordinary

organic solvents with specific viscosity  $\eta_{sp} \approx 0.08$ – $0.09$ . The structure and composition of oligomers were determined by elemental analysis, molecular masses by GPC, FTIR, and NMR spectra data. Elemental composition yields and some physical–chemical properties of oligomers are presented in Table I.

In the FTIR spectra of oligomers, one can observe characteristic bands for asymmetric valence oscillation of the linear  $\equiv\text{Si-O-Si}\equiv$  bonds at  $1020\text{ cm}^{-1}$ . In the spectra, one can see characteristic bands for  $\equiv\text{Si-Me}$ ,  $-\text{SiMe}_3$ , and for unreacted  $\equiv\text{Si-H}$  bonds at  $1275\text{ cm}^{-1}$ ,  $840\text{ cm}^{-1}$ , and  $2170\text{ cm}^{-1}$ , accordingly. In the spectra, one can observe characteristic bands for  $\text{CH}=\text{CH}$  bonds in cyclohexenyl fragment at  $1650\text{ cm}^{-1}$  and characteristic bands for cyclohexane fragments in the range  $2846$ – $2915\text{ cm}^{-1}$ .

In the <sup>1</sup>H-NMR spectra (Fig. 2) of synthesized oligomer I, one can see the singlet signals for methyl protons with chemical shift at  $\delta \approx 0.1$  and  $0.3$  ppm,

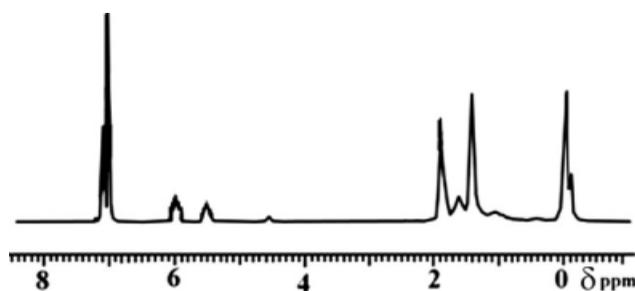


Figure 2 <sup>1</sup>H-NMR spectra of oligomer I (solvent and standard CDCl<sub>3</sub>).

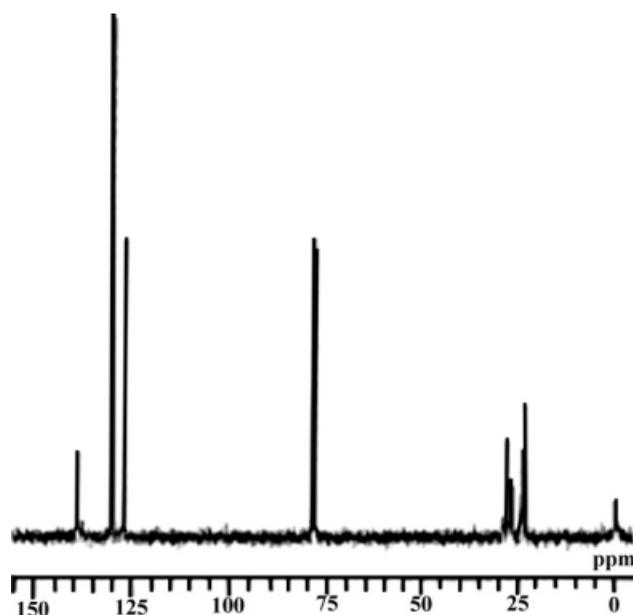
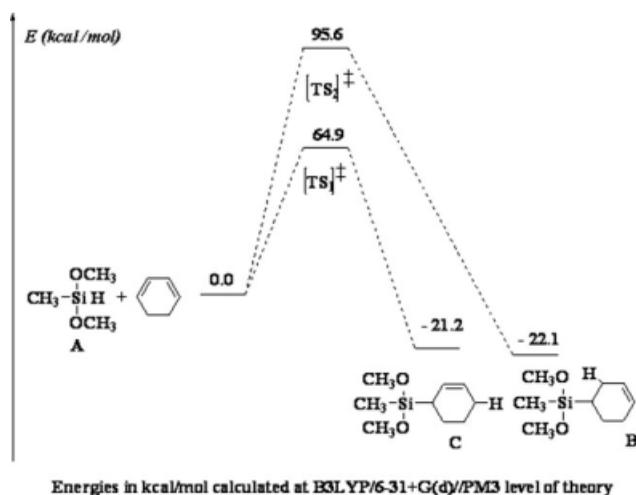


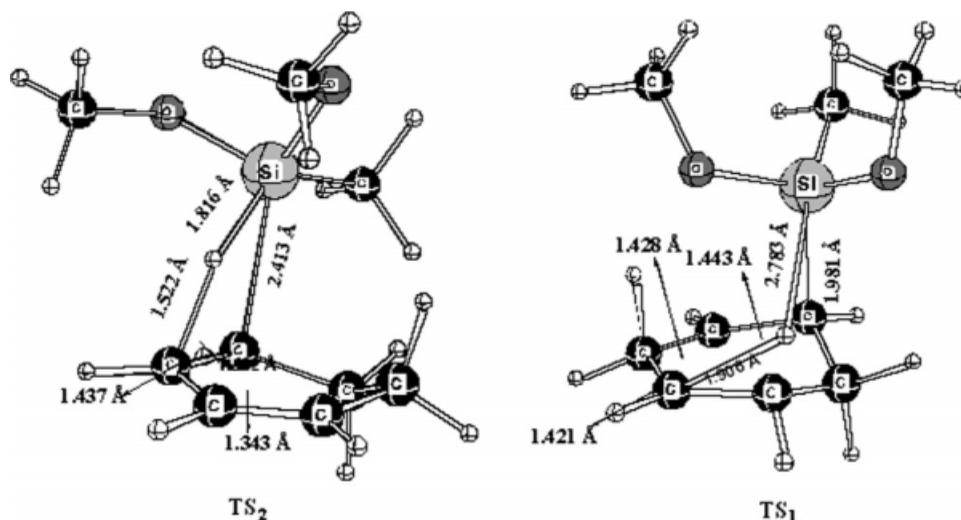
Figure 3 <sup>13</sup>C-NMR spectra of oligomer I (solvent and standard CDCl<sub>3</sub>).



**Figure 4** Relative energies for 1,2 (path A → TS<sub>2</sub> → B) and 1,4 (path A → TS<sub>1</sub> → C) addition of (MeO)<sub>2</sub>MeSiH to cyclohexa-1,3-diene.

in the spectra one can also observe broad signals for methine protons of  $-\text{CH}=\text{CH}-$  fragment, with center of chemical shift at  $\delta \approx 6.1$  and  $\delta \approx 5.5$  ppm. From spectra, it is evident that the hydrosilylation proceeds as to "1-4" direction as well as to "1-2" direction, "1-4" direction exceeds, and the ratio is  $\sim 1.6 : 1$ .

In <sup>13</sup>C-NMR spectra (Fig. 3) of oligomer I, one can observe for "1-4" and "1-2" hydride addition signals' with chemical shift: for "1-4" addition at  $\delta \approx 129.6$ ;  $\delta \approx 130.4$  ppm and for "1-2" addition at  $\delta \approx 126.7$  and  $\delta \approx 139.9$  ppm. Accordingly, the chemical shifts are easily given from saturated section characterizing for "1-4" addition at 23.7(C-1); 29.2(C-5); 27.8(C-4); 130.4(C-2); 23.7(C-1) and for "1-2" addition 24.1(C-6); 28.8(C-5); 129.6(C-4), 126.7(C-3); 22.8(C-2); 27.0(C-1).



**Figure 5** Optimized PM3 transition state geometries for the 1,2- and 1,4-addition of (MeO)<sub>2</sub>MeSiH to cyclohexa-1,3-diene, related to the reaction pathway shown in Figure 4 (TS<sub>2</sub> and TS<sub>1</sub>, respectively).

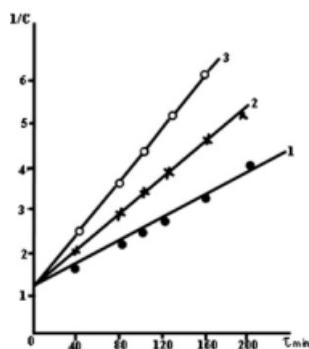
The preference for the 1,4-addition of (MeO)<sub>2</sub>MeSiH (A) to cyclohexa-1,3-diene versus 1,2-addition was supported by quantum-chemical calculation performed at B3LYP/6-31G(d)/PM3 level of theory (Fig. 4). In the Figure 4 are shown the energy profiles for the 1,2- and 1,4-addition of (MeO)<sub>2</sub>MeSiH (A) to cyclohexa-1,3-diene. One can observe that 1,2-addition is only slightly exothermic than 1,4-addition ( $-22.1$  and  $-21.2$  kcal/mole for 1,2 and 1,4 addition reactions, respectively).

On the other hand, the transition state energy for 1,4-addition (TS<sub>1</sub>) is lower by 30.7 kcal/mole than that required for the 1,2-addition (TS<sub>2</sub>). This implies that the hydrosilylation reaction will preferably follow the 1,4-addition pathway rather than energetically slightly favored 1,2-addition. The transition state geometries for 1,2 and 1,4-addition (TS<sub>1</sub> and TS<sub>2</sub>, respectively) are shown in the Figure 5.

Thus, at comparison of activation energy (the character of curve of change of energy and the value of bond orders), one can be concluded that the course of modeling reaction of hydride addition of methyl dimethoxysilane to cyclohexa-1,3-diene energetically is more favorable by 1,4-addition, that is, in agreement with NMR spectral data.

In Figure 6, the dependence of reverse concentration on the time is presented, from which it is evident that at the beginning stages the hydrosilylation reaction is of the second order. From Figure 6, the reaction rate constants at various temperatures have been calculated as follows:  $K_{60^\circ\text{C}} \approx 1.4402 \times 10^{-2}$ ,  $K_{70^\circ\text{C}} \approx 2.330 \times 10^{-2}$ , and  $K_{80^\circ\text{C}} \approx 3.2 \times 10^{-2}$  L/mol s.

From the dependence of logarithm of the reaction rate constants on the reverse temperature, the activation energy of the hydrosilylation reaction was calculated  $E_{\text{activ}} \approx 35.0$  kJ/mole. This value of

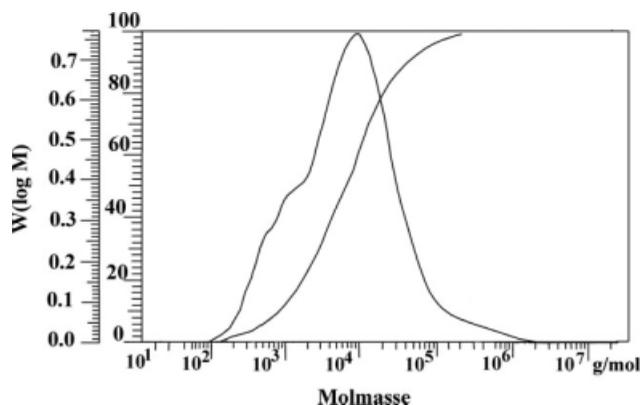


**Figure 6** Dependence of reverse concentration on the time, where curve 1 is at 60°C, curve 2 is at 70°C, and curve 3 is at 80°C.

activation energy is close to the activation energy of hydrosilylation reaction of  $\alpha,\omega$ -bis(trimethylsiloxy)-methylhydridesiloxanes to tricyclodecadiene with ( $E_{\text{activ}} \approx 32.3$  kJ/mole).<sup>9</sup>

The synthesized oligomers were studied by gel permeation chromatography. Figure 7 shows molecular weight distribution of oligomer I, which shows that the distribution has polymodal character. The average weight molecular mass of oligomer I is equal to  $48 \times 10^3$ . In case of full hydrosilylation, the value of average weight molecular masses does not exceed  $4.3 \times 10^3$ . Increased molecular mass of obtained oligomers once again proved that the reaction proceeds by macromolecular interchain hydride addition with formation of the branched oligomers. So in synthesized oligomers, the elementary links have a different structure. With the rise of reaction temperature, the intrachain and interchain hydride addition increases.

Wide-angle X-ray analyses showed that synthesized oligomers are amorphous one phase systems and value of interchain distance for oligomer I is  $d_1 = 8.43$  Å. From the Table I, one can observe that depending on the amount of cyclohexenyl groups in



**Figure 7** Gel permeation chromatographic curves of oligomer I.

the side chain, the glass transition temperature of oligomers changes in the range  $-14^\circ\text{C}$  to  $-10^\circ\text{C}$ . Increased values of glass transition temperatures in comparison with linear polydimethylsiloxane may be explained with the insertion of cyclohexenyl fragments in the chain and with the formation of partially branched systems.

Thermogravimetric investigations of oligomers have been carried out and 5% mass losses are observed at 230°C. With the rise of temperature, the mass losses increases, and above 750°C, the changes of mass losses do not occur. With the introduction of cyclohexenyl fragments in the side chain, the thermal-oxidative stability of oligomers is increased in comparison with polydimethylsiloxane polymer.

Functionalized-siloxane oligomers, which undergo rapid crosslinking reactions, are technologically important materials. These siloxanes may find specific uses in such diverse areas as elastomers, caulks, and sealing agents, adhesives, and release agents. Synthesized oligomers can be used as matrices for obtaining of new polysiloxanes on the basis of functional groups in the side chain and for modification of carbo chain elastomers.

## CONCLUSIONS

Hydrosilylations of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydrosiloxane to cyclohexa-1,3-diene 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 mainly according to 1,4-addition and not all active  $\equiv\text{Si-H}$  groups participate in the hydrosilylation reaction.

Functionalized-siloxane oligomers, which undergo rapid crosslinking reactions, are technologically important materials. These siloxanes find specific uses in such diverse areas as elastomers, caulks, and sealing agents, and adhesives.

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