

# Hydrosilylation and Dehydrocondensation Reactions of Methylhydridesiloxane to Acrylic and Methacrylic Acids

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**ABSTRACT:** The hydrosilylation of  $\alpha,\omega$ -bis(trimethylsiloxy) methylhydridesiloxane (degree of polymerization  $\approx 53$ ) with acrylic and methacrylic acid with various ratios of the initial compounds, in the presence of platinum hydrochloric acid, has been investigated. In the presence of platinum hydrochloric acid, competitive dehydrocondensation reactions take place with the formation of various oligomers with various chemical links. In the later stages of the reaction, three-dimensional systems have been obtained. During dehydro-

condensation, the reaction order, reaction rate constants, and activation energy have been determined. The structures of the synthesized oligomers have been determined with IR and NMR spectroscopy data. Gel permeation chromatography, differential scanning calorimetry, and X-ray analyses of the synthesized oligomers have been carried out. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3243–3252, 2007

**Key words:** kinetics (polym.); oligomers; polysiloxanes

## INTRODUCTION

In the literature, there is much information about the hydrosilylation of acrylic acid.<sup>1–4</sup> Petrov et al.<sup>1</sup> has shown that the hydride addition of triethylsilane to acrylic acid in the presence of Speier's catalyst proceeds in the 1,4-position with the formation of an intermediate product; by the rearrangement of this product, trimethylsilylated ether of propionic acid in a 56% yield can be obtained. The reaction proceeds according to Scheme 1.

Sadikh-Zade and Petrov<sup>2</sup> have shown that the hydrosilylation of acrylic methyl ether with triethylsilane proceeds in the 1,4-position with the formation of unsaturated silylated methyl ether.

The hydride addition of  $\alpha,\omega$ -dihydratedimethylsiloxanes to acrylic and methacrylic acids has been investigated by Andrianov and coworkers<sup>3,4</sup> in the presence of platinum hydrochloric acid ( $\text{H}_2\text{PtCl}_6$ ), and they have shown that hydrosilylation proceeds on an unsaturated C=C bond according to the Farmer rule, receiving corresponding dicarboxylic acids. The reaction proceeds according to Scheme 2 ( $\text{R} = \text{H}$  or  $\text{Me}$ , degree of polymerization = 2–11).<sup>3,4</sup> The structure of the synthesized silicon-containing

dicarbon acids has been determined with the molecular masses and IR spectroscopy data.

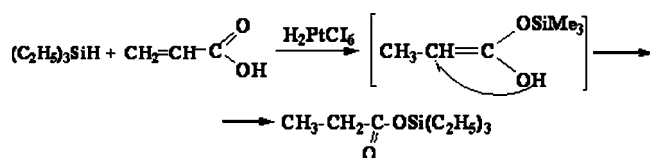
The hydrosilylation reaction of 1,4-bis(dimethylsilyl)benzene to acrylic and methacrylic acids in the presence of hydroquinone and Speier's catalyst or platinum on carbon (Pt/C) has been studied, and the reaction proceeds mainly by dehydrocondensation with the formation of corresponding acyloxysilanes according to Scheme 3 ( $\text{R} = \text{H}$  or  $\text{Me}$ ).<sup>5</sup> In hydrosilylation reactions, hydroquinone is used to prevent polymerization reactions.

The hydrosilylation reaction of methylhydridesiloxanes to unsaturated vinyl derivatives (alkenes, acrylic acid, and acrylic ethers) in the presence of Speier's catalyst has been investigated previously,<sup>6</sup> and methylsiloxane oligomers with alkyl, carboxyl, and ester side groups have been obtained according to Scheme 4 ( $\text{R} = \text{C}_n\text{H}_{2n+1}$ ,  $-\text{COOH}$ , or  $-\text{COOAlk}$ ). Moreover, catalytic dehydrocondensation between  $\equiv\text{Si}-\text{H}$ -containing compounds and hydroxyl-containing organic compounds proceeds with the isolation of hydrogen.<sup>7–9</sup> In the catalytic dehydrocondensation of hydride organosilanes with hydroxyl-containing organic compounds, catalysts such as colloid nickel, anhydrous zinc chloride, and  $\text{H}_2\text{PtCl}_6$  have been used.<sup>10,11</sup> In the dehydrocondensation of dihydride organocyclosiloxanes with dihydroxyorganocyclosiloxanes,  $\text{H}_2\text{PtCl}_6$  works, as does caustic potassium with the same activation energy.<sup>9</sup> On the other hand,  $\text{H}_2\text{PtCl}_6$  is a known catalyst of hydrosilylation.<sup>12</sup> The reaction capacity of the  $\equiv\text{Si}-\text{H}$  bond is

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**Scheme 1** Hydride addition of triethylsilane to acrylic acid.

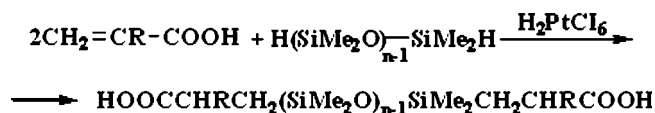
determined by the nature and amount of the catalyst, the reaction temperature, the reactant concentration, the solvent character, and so forth.<sup>7,8</sup> We have shown that during the dehydrocondensation of hydride-containing organosiloxanes with hydroxyl-containing organosilanes and siloxanes in the presence of powderlike caustic potassium as a nucleophilic catalyst, the competing reaction of dialkylsiloxane elimination does not take place.<sup>9</sup> This can be explained by a high rate of dehydrocondensation.

## EXPERIMENTAL

The starting materials for the synthesis of the comb-type methylsiloxane oligomers were  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane and acrylic and methacrylic acids.

The initial  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane, with a degree of polymerization of approximately 35, and the acrylic and methacrylic acids were obtained from Fluka (Sigma-Aldrich Chemical Company). Before the reaction, the acrylic and methacrylic acids were distilled. The organic solvents used in hydrosilylation were cleaned by drying and distillation.

IR spectra of all the samples were taken on a UR-20 instrument (Zeiss Jena) from KBr pellets, whereas the <sup>1</sup>H-NMR spectra were taken on a Perkin-Elmer instrument (Perkin-Elmer R34 spectrometer, Perkin-Elmer, USA) at an operating frequency of 250 MHz. All spectra were obtained with CDCl<sub>3</sub> as the solvent and internal standard. A Perkin-Elmer DSC-2 differential scanning calorimeter was used to perform ther-



**Scheme 2** Hydride addition of  $\alpha,\omega$ -dihydratedimethylsiloxanes to acrylic and methacrylic acid.

mogravimetric analysis, and the thermal transitions (glass-transition temperatures) were read at the maxima of the endothermic or exothermic peaks. The heating and cooling scanning rate was 10°C/min.

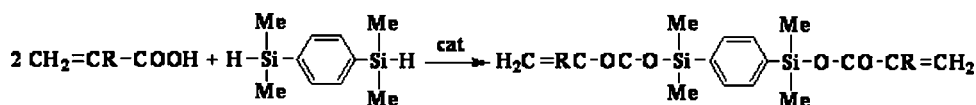
A gel permeation chromatography (GPC) investigation was carried out with a Waters model 6000A (Waters, USA) chromatograph and an R 401 differential refractometer detector. The column set comprised 10<sup>3</sup>- and 10<sup>4</sup>-Å Ultrastayragel columns. The sample concentration was approximately 3 wt % in toluene, and the typical injection volume for the siloxane was 5 μL. The GPC standardization was accomplished with styrene or polydimethylsiloxane standards of known molecular weights.

Wide-angle X-ray diffractograms were taken on a DRON-2 instrument (Burevestnik, St. Petersburg, Russia). Cu K $\alpha$  was measured without a filter, and the angular velocity of the motor was approximately 2°/min.

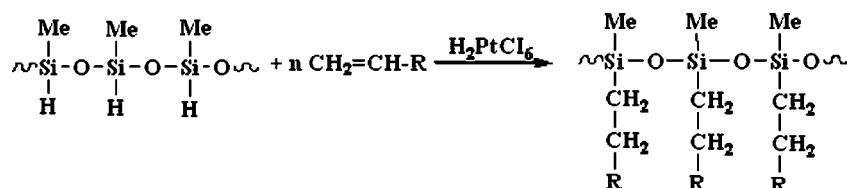
## Dehydrocondensation of $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane with acrylic acid

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

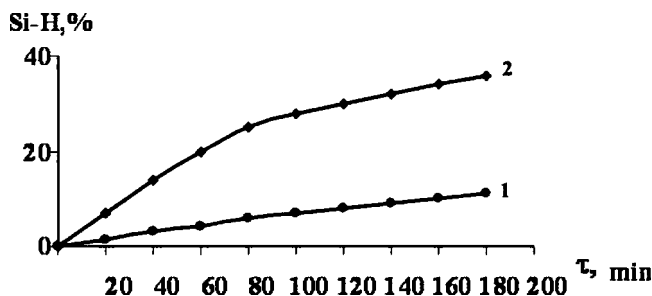
The reaction products were placed in the flask and thermostated in an oil bath until a constant temperature was achieved. Then, a 0.1M catalyst solution of H<sub>2</sub>PtCl<sub>6</sub> in tetrahydrofuran (5–9 × 10<sup>-5</sup> g/g of the starting substance) was introduced. After that, hydrogen release was started; hydrogen was collected in the gasometer. After the reaction was finished 5 mL of



**Scheme 3** Hydrosilylation reaction of 1,4-bis(dimethylsilyl)benzene to acrylic and methacrylic acid.



**Scheme 4** Hydrosilylation reaction of methylhydridesiloxanes to unsaturated vinyl derivatives.



**Figure 1** Dependence of the changes in the percentage of active  $\equiv\text{Si}-\text{H}$  groups on the time for the dehydrocondensation reaction of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to acrylic acid at  $60^\circ\text{C}$ : (1) catalyst Pt/C and (2) catalyst  $\text{H}_2\text{PtCl}_6$ ,  $t$ , time.

anhydrous toluene was added; the solution was filtered, and the solvent was eliminated.

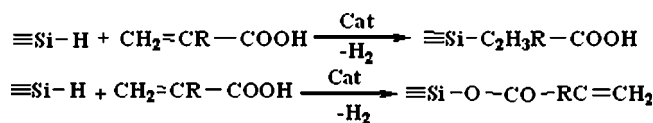
#### Hydride addition of $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to acrylic acid

The hydrosilylation reaction was carried out in a three-necked flask equipped with a stirrer, a reflux condenser, and a calcium chloride drying tube. The initial reagents were placed in the flask and thermostated in an oil bath until a constant temperature was achieved. A  $0.1\text{M}$  solution of  $\text{H}_2\text{PtCl}_6$  in tetrahydrofuran ( $5-9 \times 10^{-5}$  g/g of the starting substance) was used as a catalyst. The reaction was carried out in an argon atmosphere in an anhydrous toluene solution at  $60^\circ\text{C}$ . Then, 5 mL of anhydrous toluene was added to the reaction mixture, which was filtered and connected to a vacuum; the toluene and unreacted acrylic acid were removed at  $30-40^\circ\text{C}$ .

The hydrosilylation reaction in the presence of Pt/C was carried out in the same manner.

### RESULTS AND DISCUSSION

As a review of the literature has shown, the hydride-addition reactions of  $\equiv\text{Si}-\text{H}$ -bond-containing compounds with acrylic and methacrylic acids proceed in different directions. This article deals with the synthesis and studies of the properties of comb-type organosiloxanes containing carboxyl groups in the side chains.



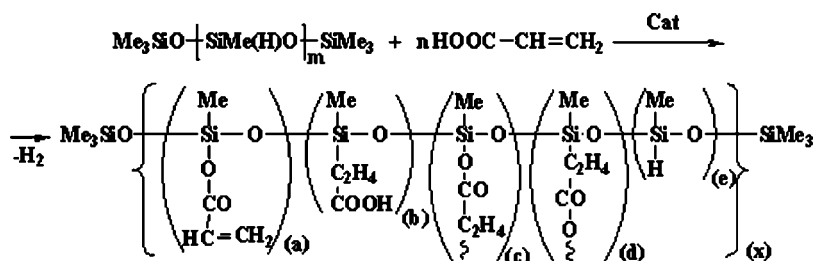
**Scheme 5** Possible hydrosilylation and dehydrocondensation reactions of methylhydridesiloxane to acrylic and methacrylic acids.

For the synthesis of organosiloxane oligomers with carboxyl groups in the side chains, the hydride addition of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxanes (degree of polymerization  $\approx 35$ ) to acrylic and methacrylic acids with a 1 : 35 ratio of the initial compounds in the presence of catalyst  $\text{H}_2\text{PtCl}_6$  or Pt/C (5%) at various temperatures in dry toluene solutions (50–60%; i.e., melt conditions) has been investigated.

The preliminary heating of the initial compounds for 4 h in the presence of a  $0.1\text{M}$   $\text{H}_2\text{PtCl}_6$  solution in tetrahydrofuran ( $\sim 5-9 \times 10^{-5}$  g/g of the reaction substances) in the temperature range of  $50-70^\circ\text{C}$  has shown that the polymerization of acrylic or methacrylic acids, the breaking of siloxane backbones, the elimination of methane or hydrogen in the methylhydridesiloxanes, and other changes do not take place. Besides, there are no changes in the NMR spectra of the initial compounds. As known from the literature,<sup>13</sup>  $\text{H}_2\text{PtCl}_6$ , except for hydrosilylation, catalyzes the dehydrocondensation reaction. Therefore, for the complete characterization of the process during the reaction, the conversation of hydrogen has been observed.

Hydrosilylation has been investigated without a solvent in the presence of catalysts at  $70^\circ\text{C}$ , and it has been found that in the early stages of hydrogen conversion ( $\sim 10-20\%$ ), the reaction proceeds with the formation of three-dimensional systems. In this case, the depth of the hydrosilylation reaction is approximately 60%. To prevent the crosslinking processes, the reactions have been conducted in a dry toluene solution.

During the reaction in solution, at a hydrogen conversion of approximately 35% (Fig. 1), the crosslinking processes take place. By the determination of the active  $\equiv\text{Si}-\text{H}$  groups from the soluble parts of the reaction products, it has been established that the depth of hydrosilylation is approximately 50%. This indicates that in the presence of  $\text{H}_2\text{PtCl}_6$ , in a dilute solution of toluene, besides hydrosilylation, approxi-



**Scheme 6** Hydrosilylation and dehydrocondensation reactions of methylhydridesiloxane with acrylic acid.

TABLE I  
Some Physical and Chemical Properties and Yields of the Branched Oligomers

Oligomer	Yield (%)	Ratio	$\eta_{sp}^a$	H <sub>2</sub> Conversion (%)	Depth of hydrosilylation (%)	$d_1$ (Å)	$M_w$ ( $\times 10^{-3}$ ) <sup>b</sup>	$T_g$ (°C) <sup>c</sup>
I	57	1 : 35	0.08	30	50	8.85	7.2	-67
II	49	1 : 17.5	0.06	23	49	—	—	—
I <sup>1</sup>	66	1 : 35	0.08	10	54	8.23	—	-70
III	13	—	0.07	—	—	8.92	60.8	-23

<sup>a</sup> Specific viscosity in a 1% solution of toluene at 25°C.

<sup>b</sup> Weight-average molecular weight.

<sup>c</sup> Glass-transition temperature.

mately 30% dehydrocondensation occurs concurrently (Fig. 1, curve 1).

For the purpose of synthesizing oligomers that are easily dissolved in organic solvents, the same reaction has been studied in the presence of Pt/C (5%) in a dry toluene solution: dehydrocondensation proceeds with less activity (9–10%; Fig. 1, curve 2), but three-dimensional systems are obtained. Hydrosilylation under these conditions proceeds to an extent of approximately 54%. Therefore, in both cases, the reaction proceeds in two concurrent ways, with the formation of various linked oligomers, according to Scheme 5. With an increase in the dilution of the reaction solution, the hydrosilylation and dehydrocondensation rates decrease, but the soluble part of the reaction products increases. Generally, the reaction proceeds according to Scheme 6  $\{m \approx 35 = [(a) + (b) + (c) + (d) + (e)]x(x)$ ; with H<sub>2</sub>PtCl<sub>6</sub> as the catalyst, the ratio for I is 1 : 35, and the ratio for II is 1 : 17.5; with Pt/C as the catalyst, the ratio for I<sup>1</sup> is 1 : 35}. From the crosslinked polymers, the soluble part has been isolated in a yield of approximately 50–66%. They are colorless, transparent, viscous products soluble in ordinary organic, aromatic-type solvents. Some physicochemical properties and yields of the synthesized branched oligomers are presented in Table I.

For a time, the synthesized oligomers undergo a self-catalyzed structuring process. From oligomer I after 24 h, soluble part III has been isolated in a yield of approximately 13%.

For oligomer III, an investigation has been carried out with <sup>1</sup>H- and <sup>13</sup>C-NMR. In Figure 2, we can observe a triplet signal, with a chemical shift at  $\delta \approx 1.25$  ppm ( $J = 6.0$  Hz), which is characteristic of hydrogen protons in the  $\equiv\text{Si}-\text{CH}_2-$  group. We can also see a triplet signal for hydrogen protons in the  $-\text{CH}_2-\text{CO}-$  group with a chemical shift at  $\delta \approx 2.5$  ppm and singlet signals with chemical shifts at  $\delta \approx 0.1$  ppm and  $\delta \approx 0.3$  ppm for methyl protons in the  $-\text{SiMe}_3$  and  $\equiv\text{SiMe}$  groups, respectively. In the spectra, we can see complicated multiplets characteristic of vinyl groups with a chemical shift at  $\delta \approx 5.80$ – $6.1$  ppm; this indicates that the reaction proceeds partially by dehydrocondensation. There is a low-intensity singlet signal at  $\delta \approx 4.2$  ppm that is characteristic of an unreacted  $\equiv\text{Si}-\text{H}$  bond. We can also see a characteristic signal for residual acid protons with a chemical shift at  $\delta \approx 10.2$  ppm and multiplet signals of phenyl protons in toluene with a chemical shift at  $\delta \approx 7.2$ – $7.6$  ppm; these indicate traces of toluene in the synthesized oligomers.

The <sup>13</sup>C-NMR spectrum of oligomer III (Fig. 3) shows a signal for carbon in the residual acid carbonyl group with a chemical shift at  $\delta \approx 179.3$  ppm, a signal with a chemical shift at  $\delta \approx 7.5$  ppm in the  $\equiv\text{SiMe}$  group, a signal with a chemical shift at  $\delta \approx 6.9$  ppm in  $-\text{SiMe}_3$ , a signal with a chemical shift at  $\delta \approx 25.9$  ppm characteristic of carbon in the  $\equiv\text{Si}-\text{CH}_2-$  group, and a signal with a chemical shift at  $\delta \approx 27.5$  ppm characteristic of carbon in the methylene group in the  $-\text{CH}_2-\text{COOH}$  fragment. The reaction in the other direction by dehydrocondensation is proved by the

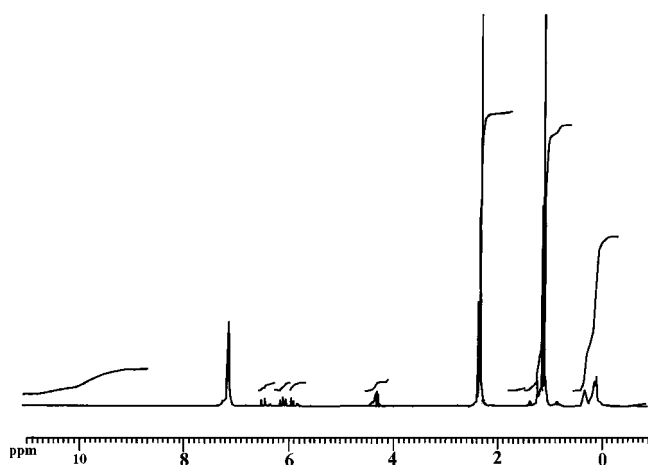


Figure 2 <sup>1</sup>H-NMR spectrum of oligomer III (solvent and standard CDCl<sub>3</sub>).

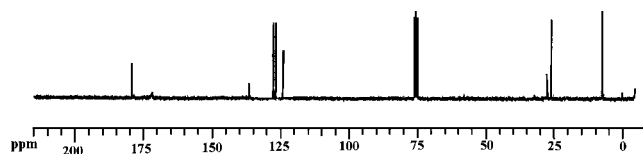
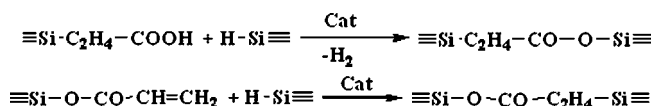


Figure 3 <sup>13</sup>C-NMR spectrum of oligomer III (solvent and standard CDCl<sub>3</sub>).



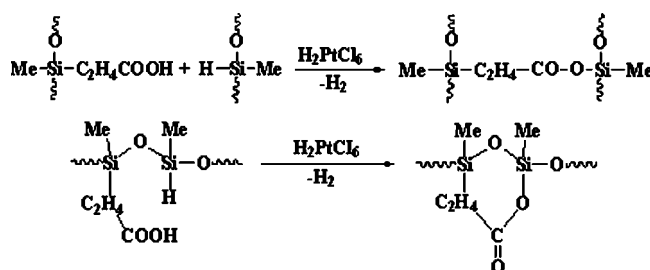
**Scheme 7** Possible intermolecular hydrosilylation and dehydrocondensation reactions.

presence in the  $^{13}\text{C}$ -NMR spectrum of a signal with a chemical shift at  $\delta \approx 171.7$  ppm, which is characteristic of free carbon from a proton carboxyl group ( $\equiv\text{Si}-\text{O}-\text{CO}-$ ). The obtained crosslinked systems can be explained by intermolecular hydrosilylation and dehydrocondensation (Scheme 7).

In the IR spectra of the oligomers, we can see the absorption bands characteristic of the  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  and  $\equiv\text{Si}-\text{O}-\text{C}\equiv$  bonds at  $1020$  and  $1080\text{ cm}^{-1}$ . We can also see the absorption bands for  $\equiv\text{SiMe}$  and for unreacted  $\equiv\text{Si}-\text{H}$  bonds, an intensive signal for carbonyl etheral groups, and signals for double bonds at  $1275$ ,  $2165$ ,  $1720$ , and  $1640\text{ cm}^{-1}$ .

In the IR spectra, there are no absorption bands characteristic of associated and unassociated hydroxyl groups. Therefore, the hydroxyl group takes part in intermolecular dehydrocondensation, as stated previously, and this leads to the formation of three-dimensional or crosslinked systems and intramolecular cyclization according to Scheme 8 [ $-\text{C}_2\text{H}_4- = -(\text{CH}_2)_2-$ ]. On the other hand, if the reaction proceeds by dehydrocondensation, for the synthesized oligomers, resonance signals for unsaturated vinyl fragments, with chemical shifts in the range of  $5.5$ – $6.2$  ppm, must be observed. However, in the spectra of Figures 2 and 3, there are low-intensity resonance signals, which show that the  $\equiv\text{Si}-\text{O}-\text{CO}-\text{CH}=\text{CH}_2$  fragment can enter by intramolecular and intermolecular hydride addition in agreement with Scheme 9 [ $-\text{C}_2\text{H}_4- = -(\text{CH}_2)_2-$ ]. For oligomers I and III, a wide-angle X-ray investigation has been carried out. The oligomers are represented as one-phase amorphous products, for which the value of the interchain distances changes in the range of  $d_1 \approx 8.23$ – $8.92\text{ \AA}$ .

The synthesized oligomers have been studied with GPC. Figure 4 shows the GPC curves of the soluble parts of oligomers I and III, which are sharply dis-

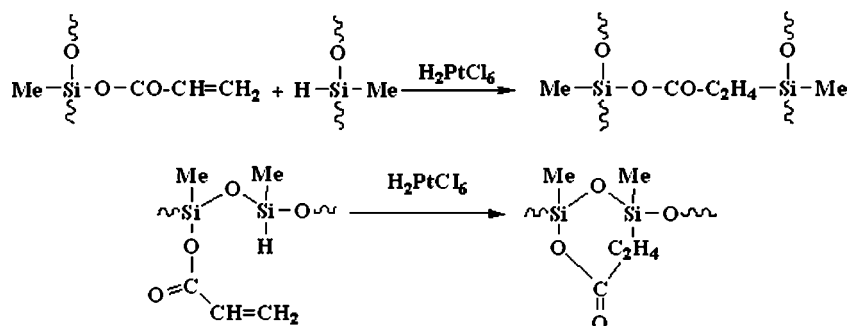


**Scheme 8** Possible intermolecular and intramolecular dehydrocondensation reactions.

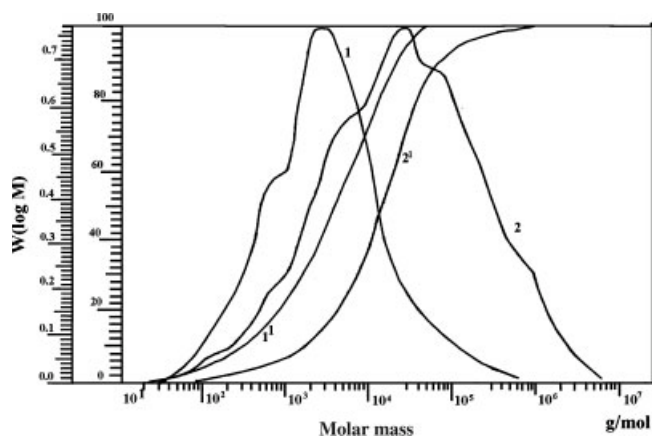
tinguished from each other. The molecular weight distribution of oligomer I has a bimodal character (Fig. 4, curve 1), and for oligomer III, it has a polymodal character (Fig. 4, curve 2); therefore, it is evident that during hydrosilylation, dehydrocondensation takes place, in contrast to earlier published data.<sup>3,4</sup> The weight-average molecular weight of oligomer I is approximately  $7.2 \times 10^3$ , and the polydispersity is approximately 9.4. For irregularly branched oligomer III, the weight-average molecular weight is approximately  $60.8 \times 10^3$ , and the polydispersity is approximately 35.3.

An analogous hydrosilylation reaction of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to methacrylic acid in the presence of the catalyst  $\text{H}_2\text{PtCl}_6$  (a  $0.1\text{M}$  solution in tetrahydrofuran) with a  $1 : 35$  ratio of the initial compounds at various temperatures in both a melt and in a dry toluene solution ( $50$ – $60\%$ ) has been investigated.

At  $40^\circ\text{C}$ , with  $2\%$  hydrogen conversion, crosslinking takes place. From the soluble part of the crosslinked products through the determination of the concentration of active  $\equiv\text{Si}-\text{H}$  groups, it has been established that the depth of hydrosilylation is approximately  $84\%$ . With an increase in the temperature from  $50$  to  $60^\circ\text{C}$ , the dehydrocondensation part of the reaction increases from approximately  $3.8$  to approximately  $15.0\%$  (see Fig. 5). The hydrosilylation part of the reaction at  $60^\circ\text{C}$  is equal to approximately  $82\%$ . Therefore, during the reaction of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to methacrylic acid in the presence of the catalyst  $\text{H}_2\text{PtCl}_6$ , besides hydrosilylation (in both direc-



**Scheme 9** Possible intermolecular and intramolecular hydrosilylation reactions.



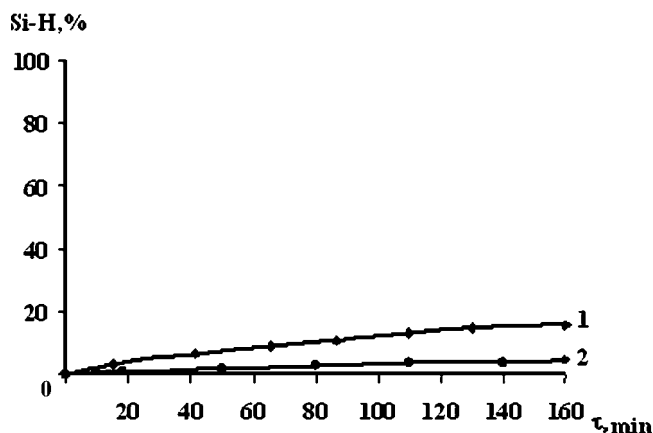
**Figure 4** GPC curves of the oligomers: (1) oligomer I and (2) oligomer III. *W*, molecular weight; *M*, molecular mass.

tions: the Farmer rule and the Markovnikov rule), catalytic dehydrocondensation takes place.

During the dilution, the depth of the dehydrocondensation and hydrosilylation reactions decreases, and the yield of the soluble part rises. The reaction of methylhydridesiloxane with methacrylic acid proceeds with the formation of various linked products according to Scheme 10 [(a) + (b) + (c) + (d) + (e) + (f) + (g)](*x*) = *n*; the temperature is 40°C for IV<sup>1</sup>, 50°C for IV<sup>2</sup>, and 60°C for IV<sup>3</sup>. From the crosslinked polymers, the obtained branched oligomers are viscous products that easily dissolve in aromatic solvents, with a specific viscosity of approximately 0.04–0.06. Some physicochemical properties and yields of oligomers IV<sup>1</sup>–IV<sup>3</sup> are presented in Table II.

The synthesized oligomers have been studied with <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. According to the spectroscopy data for the reaction products, we propose that, in general, the hydride addition of methylhydridesiloxane to acrylic and methacrylic acids can proceed in several different ways (see Scheme 11).

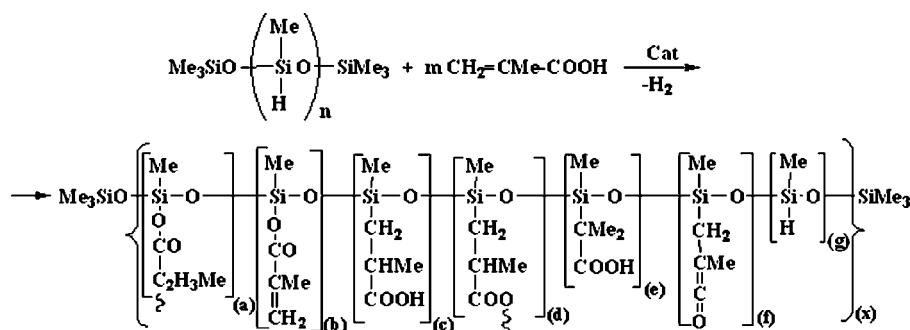
In the <sup>1</sup>H-NMR spectrum of oligomer IV<sup>3</sup>, we can observe a singlet signal with a chemical shift at δ ≈ 1.21 ppm for methyl protons in the =CH–Me group, a broadened singlet signal for methyl protons in the C–Me group, a signal with a chemical shift at δ ≈ 1.22 ppm for the α-addition product [Markovnikov



**Figure 5** Dependence of the changes in the percentage of active ≡Si–H groups on the time for the dehydrocondensation reaction of α,ω-bis(trimethylsiloxy)methylhydridesiloxane to methacrylic acid at 60°C: (1) 50 and (2) 60°C (in the presence of H<sub>2</sub>PtCl<sub>6</sub>). *t*, time.

rule; Scheme 11(2)], a signal with a chemical shift at δ ≈ 0.8 ppm for protons of the methylene group, and a β-addition product in the ≡Si–CH<sub>2</sub>– fragment, the creation of which can be examined as a structure obtained by the regrouping of the intermediate product [transition complex; 1,4-addition according to the Eltekov rule; Scheme 11(3a)].

The structure of the product obtained by Scheme 1(3a) is similar to the structure of the product obtained by the Farmer rule (1,2-addition). The chemical shifts and multiplicity of the remaining protons are as follows: for the methine group (≡CH), a sextet (*R* = Me) with δ ≈ 2.6 ppm (*J* = 6.83 Hz); for the methyl group, a singlet at δ ≈ 1.21 ppm (*J* = 7.07 Hz); and for the protons in the carboxyl group, a broadened signal with a chemical shift at δ ≈ 10–11 ppm. For another reaction course, after which the elimination of water molecules according to Scheme 1(3) takes place, with the formation of ketene groups, the chemical shifts are as follows: for protons in the methylene ≡Si–CH<sub>2</sub>– group, a singlet signal with a chemical shift at δ ≈ 0.78 ppm, and for the methyl protons in the –CMe=C=O fragment, a singlet signal with a chemical shift at δ ≈ 1.96 ppm. It has been suggested that the direction of the



**Scheme 10** Hydrosilylation and dehydrocondensation reactions of methylhydridesiloxane with methacrylic acid.

TABLE II  
Some Physical and Chemical Properties and Yields of Oligomers IV<sup>1</sup>–IV<sup>3</sup>

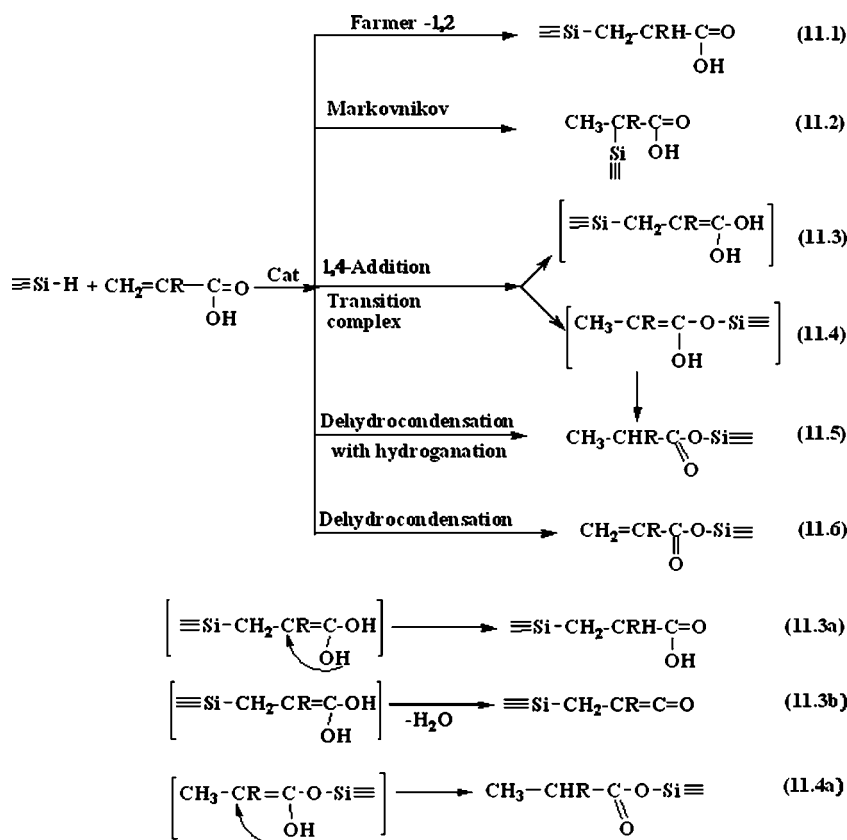
Oligomer	Yield (%)	Ratio	$\eta_{sp}^a$	Reaction temperature (°C)	Conversion of H <sub>2</sub> (%)	Hydrosilylation (%)	$d_1$ (Å)
IV <sup>1</sup>	68	1 : 35	0.04	40	2.0	84	—
IV <sup>2</sup>	66	1 : 35	0.05	50	3.8	88	—
IV <sup>3</sup>	64	1 : 35	0.06	60	15	82	9.07

<sup>a</sup> Specific viscosity in a 1% solution of toluene at 25°C.

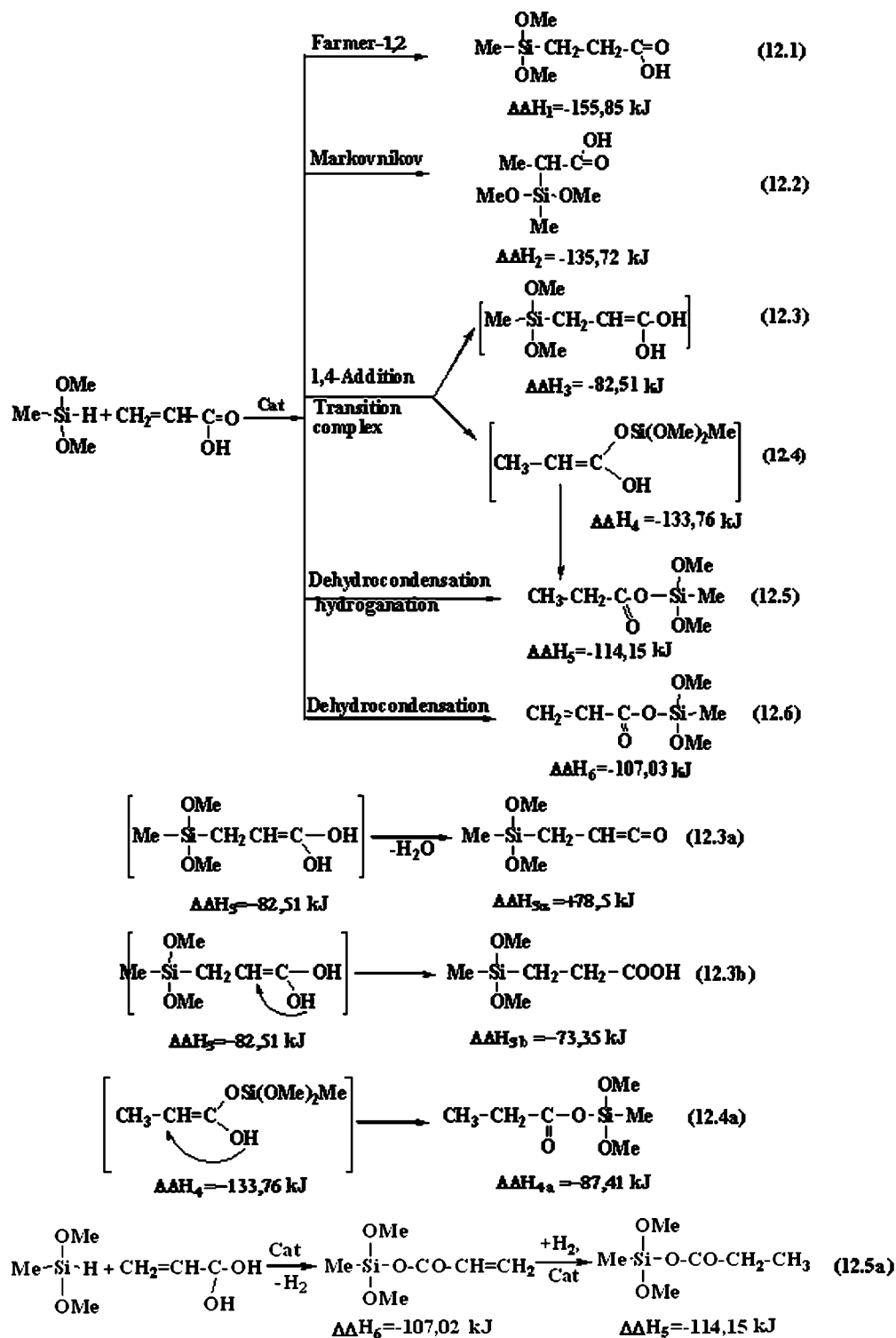
reaction with the acquisition of the transition complex agrees with Scheme 11(4).<sup>1</sup> The obtained transition complex then undergoes regrouping according to Scheme 11(4a), and a simultaneous dehydrocondensation–hydrogenation product is obtained, in agreement with Scheme 11(5). However, processing the reaction according to the aforementioned scheme is improbable because released hydrogen during the dehydrocondensation reaction is eliminated from the reaction mixture.

The acquisition of three hydrosilylation products with methacrylic acid has been proved by <sup>13</sup>C-NMR spectroscopy. Each of the adducts is characterized by the following chemical shifts. For the hydrosilylation product by the Markovnikov rule [Scheme 1(2)], we can observe a resonance signal for methyl protons at  $\delta \approx 18.11$  ppm, a signal for the quaternary carbon nucleus at  $\delta \approx 34.11$  ppm, and a signal for the carbon nucleus in the carboxyl group at  $\delta \approx 172.74$  ppm. For the hydrosilylation product by the Farmer rule [1,2-addition; Scheme 11(1)], we can observe a signal for the carbon nucleus with a chemical shift at  $\delta \approx 18.98$  ppm in the  $\equiv\text{Si}-\text{CH}_2-$  fragment, a signal at  $\delta \approx 29.58$  ppm for the carbon nucleus in the  $=\text{CH}-$  group, and a signal for the methyl group at  $\delta \approx 22.92$  ppm in the  $\text{Me}-\text{CH}-$  fragment.

We can observe analogous values of the signals for the compound containing ketene groups: a signal with a chemical shift at  $\delta \approx 18.98$  ppm characteristic of the carbon nucleus of the methylene group ( $\equiv\text{Si}-\text{CH}_2-$ ), a signal at  $\delta \approx 30.2$  ppm for carbon in the methyl group [ $-\text{C}(\text{Me})=\text{C}=\text{O}$ ], a signal for the tertiary carbon nucleus at  $\delta \approx 135.6$  ppm [ $-\text{C}(\text{Me})=\text{C}=\text{O}$ ], and a signal at  $\delta \approx 183.43$  ppm for the carbon nucleus in the  $=\text{C}=\text{O}$  group.



Scheme 11 Possible scheme of the hydrosilylation of methylhydridesiloxane to acrylic and methacrylic acids.



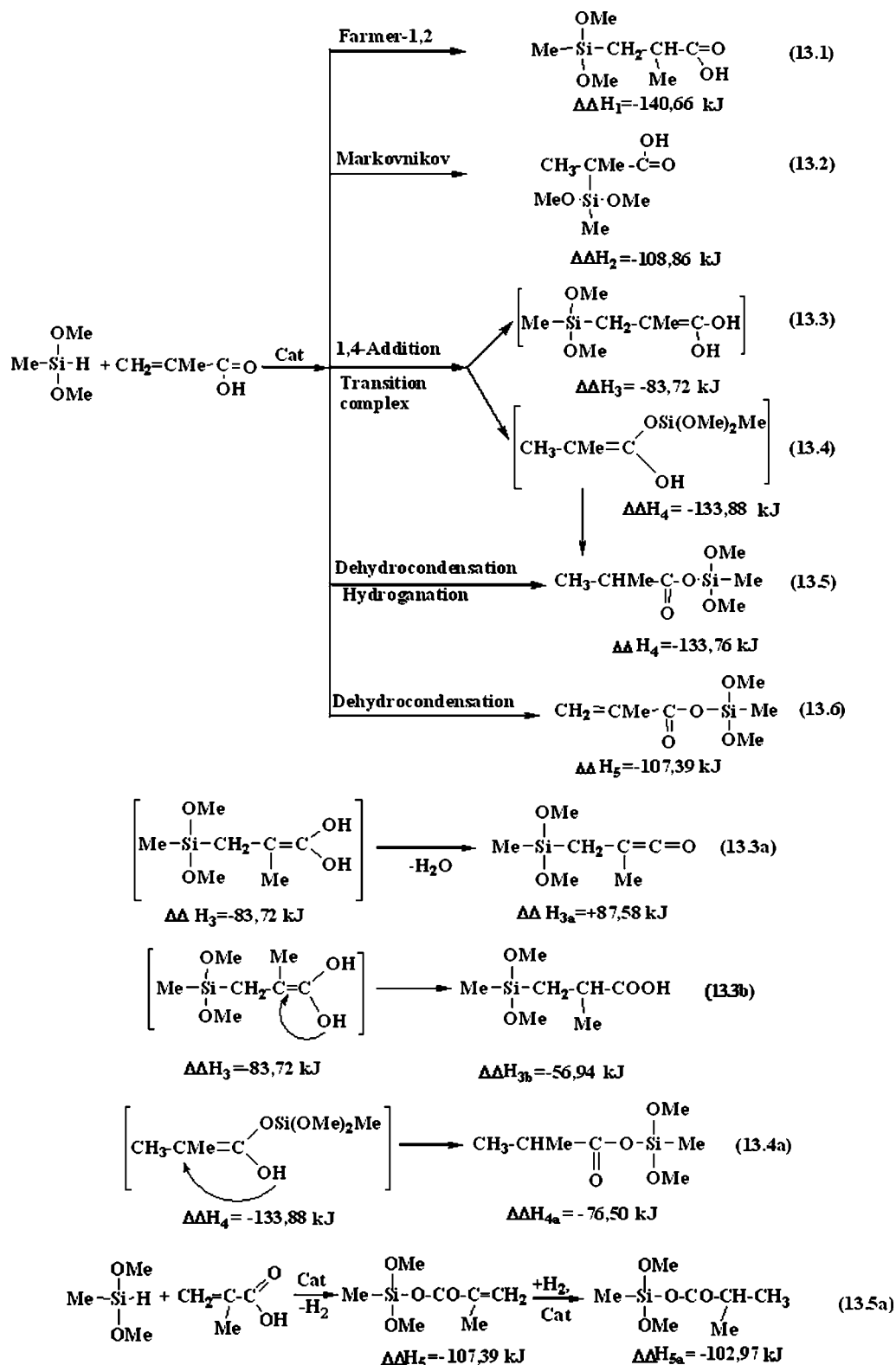
**Scheme 12**  $\Delta\Delta H$  for the model hydrosilylation and dehydrocondensation reactions of methyltrimethoxysilane with acrylic acid. Part 5a presents a model dehydrocondensation–hydrogenation reaction of methyltrimethoxysilane with acrylic acid.

The hydrosilylation reactions of methylhydridesiloxanes to acrylic and methacrylic acids are distinguished from each other in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy data and in the literature data.<sup>1</sup> With acrylic acid, hydrosilylation mainly proceeds by dehydrocondensation

and hydrosilylation [Farmer rule (Scheme 11(1,3a)]. In contrast, hydrosilylation to methacrylic acid proceeds in almost all directions, as presented in Scheme 11.

For the full characterization of the hydride addition of methylhydridesiloxane to acrylic and metha-





**Scheme 13**  $\Delta\Delta H$  for the model hydrosilylation and dehydrocondensation reactions of methyltrimethoxysilane with methacrylic acid. Part 5a presents a model dehydrocondensation–hydrogenation reaction of methyltrimethoxysilane with methacrylic acid.

acrylic acids by the quantum–chemical, half-empirical Austin Model 1 method,<sup>14</sup> for all initial, intermediate, and final products, for the model reaction of

hydrosilylation of methyltrimethoxysilane to acrylic and methacrylic acids, we have calculated the heat of formation ( $\Delta H_f$ ) and change in the enthalpy

( $\Delta\Delta H$ ) proceeding in various concurrent ways (Scheme 12). Scheme 12 shows that starting from the calorific effects of all possible directions of the hydrosilylation reaction of methyltrimethoxysilane to acrylic acid is thermodynamically the more profitable course of the reaction according to the Farmer rule (1,2-addition). The product obtained by the regrouping of the intermediate product [1,4-addition, Scheme 12(3)], similarly to the Eltekov rule [Scheme 12(3b)], is identical to the product obtained by the Farmer rule [Scheme 12(1)], and they have the same calorific effects [ $\Delta\Delta H_1 = \Delta\Delta H_3 + \Delta\Delta H_{3a} = -82.51 \text{ kJ} + (-73.35 \text{ kJ}) = -135.85 \text{ kJ}$ ]. Obtaining ketene by the regrouping of the intermediate product according to Scheme 12(3a) is most probable.

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy data for oligomer III show that in the hydrosilylation of methylhydridesiloxanes to acrylic acids, ketenes are not obtained.

The structure of the product obtained by dehydrocondensation–hydrogenation reactions [Scheme 12(5)] is identical to the product obtained by the regrouping of the intermediate product [Scheme 12(4a)] according to the Eltekov rule. Scheme 12(5a) is a possible reaction. The structure of the product obtained in this way is identical to the structure of the product obtained by the regrouping of the intermediate product [Scheme 12(4)] according to Scheme 12(5a), and they have the same calorific effects ( $\Delta\Delta H = \Delta\Delta H_4 + \Delta\Delta H_{4a} = \Delta\Delta H_6 + \Delta\Delta H_5 = -221.17 \text{ kJ}$ ). The course of the reaction according to Scheme 12(4,4a), compared with the other course, is energetically profitable. The dehydrocondensation–dehydrogenation course of the reaction according to Scheme 12(5a) is improbable because during dehydrocondensation, released hydrogen is isolated from the reaction mixture; that is, it is fixed from the reaction mixture during the process, but a strong denial of the course of the reaction in Scheme 12(5a) is impossible. Besides, it is possible that the sensitivity of the instrument and the conditions of the obtained spectra are insufficient for the identification of all possible products obtained at a low concentration.

Scheme 13 shows  $\Delta\Delta H$  for all the reactions proceeding in various concurrent ways during the model hydrosilylation reaction of methyltrimethoxysilane to methacrylic acid. Under the assumption of the heat of the model reaction of methyltrimethoxysilane with methacrylic acid (Scheme 13), hydrosilylation according to the Farmer rule (1,2-addition) is thermodynamically more profitable. The structure of the product obtained by the regrouping of the transition complex [1,4-addition; Scheme 13(3)] according to the Eltekov rule [Scheme 13(3a)] is similar to the structure of the product obtained by the Farmer rule. Their heat of

reaction ( $\{\Delta\Delta H_1 = \Delta\Delta H_3 + \Delta\Delta H_{3b} = [-83.72 \text{ kJ} + (-56.94 \text{ kJ})] = -140.66 \text{ kJ}\}$ ) is the same too. The formation of the ketene group from the transition complex according to Scheme 13(3a) is most probable because its heat of reaction is equal to  $\Delta\Delta H_{3a} = +87.58 \text{ kJ}$ . Despite this, in contrast to acrylic acid, ketene groups are obtained in methacrylic acid, as proved by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy data.

The dehydrocondensation–dehydrogenation reaction of methyltrimethoxysilane with methacrylic acid is more comprehensively presented in Scheme 13(5a). Analogously, the course of the reaction according to Scheme 13(5) is improbable, although its exclusion is not possible.

Wide-angle X-ray analyses of oligomer IV<sup>3</sup> have shown that the oligomer is a one-phase amorphous system with  $d_1 \approx 9.07 \text{ \AA}$ .

Therefore, for the first time, hydride-addition reactions of methylhydridesiloxane to acrylic and methacrylic acids have been studied in the presence of catalysts  $\text{H}_2\text{PtCl}_6$  and  $\text{Pt/C}$ , and the results differ from the literature data. Besides hydrosilylation reactions (1,2- and 1,4-addition), dehydrocondensation reactions take place with the formation of various linked, thermoreactive oligomers.

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