

# Hydrosilylation Reaction of Methylhydridesiloxane to Phenylacetylene

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Received 1 March 2005; accepted 29 August 2005

DOI 10.1002/app.23664

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

**ABSTRACT:** The hydrosilylation reaction of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to phenylacetylene in the presence of catalyst—platinum hydrochloric acid (0.1M solution in tetrahydrofuran)—at 1 : 35 ratio of initial compounds, at various temperatures (40–60°C) was investigated and methylsiloxane oligomers with phenethenyl substituted groups in the side chain has been obtained. It was shown that complete hydrosilylation of all active (Si—H groups do not take place. The hydrosilylation reaction order, activation energy, and rate constants were found. The syn-

thesized oligomers were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectral data. Gel-permeation chromatographic, differential scanning calorimetric, thermogravimetric, and wide-angle X-ray investigations of synthesized oligomers were carried out. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2511–2515, 2006

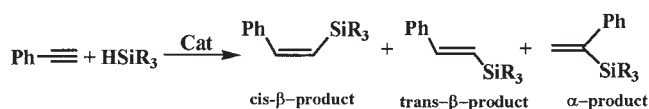
**Key words:** methylhydridesiloxane; phenylacetylene; hydrosilylation; hydride addition

## INTRODUCTION

The properties of organosilicon polymers depend on the structure of the macromolecular chain and on the nature of organic groups surrounding the silicon atom.<sup>1</sup> Great attention has been paid to copolymers, where different organic substituted groups are bonded to methylsiloxane hydrophobic matrix. By varying these substituted groups, it is possible to utilize the aforementioned copolymers in a wide range.

The hydrosilylation continues to be much studied and reviewed, and the role of transition metal catalysts represents a key aspect of these studies. The results of such investigations revealed that product distributions vary considerably with the nature of the acetylene, the silane structure, the catalyst and the reaction conditions.<sup>2</sup>

There are reports of the hydride addition reactions of silanes to phenylacetylene using  $\text{H}_2\text{PtCl}_6$  as a catalyst resulting in the predominant formation of the *trans*- $\beta$ -addition products (via *cis*-addition)  $t\text{-R}_3\text{SiCH}=\text{CHPh}$ , with minor formation of the  $\alpha$ -products  $\text{R}_3\text{Si(Ph)C}=\text{CH}_2$ . Few *cis*- $\beta$ -products derived from *trans*-addition are observed using this catalytic system. The *cis*-addition occurs with retention of configuration at Si atom<sup>3–7</sup>:

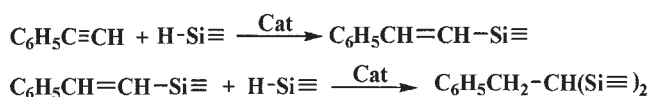


The hydride addition reactions of  $\text{Ph}_2\text{MeSiH}$  and  $\text{PhMe}_2\text{SiH}$  to phenylacetylene in the presence of  $\text{H}_2\text{PtCl}_6/\text{CO}$  catalytic system are known. It was shown that the ratio between obtained products in the case of  $\text{PhMe}_2\text{SiH}$  is  $\alpha : \text{trans-}\beta = 66 : 34$  (in the absence of CO it is equal to 25 : 75). In the case of  $\text{Ph}_2\text{MeSiH}$ , the ratio between obtained products is  $\alpha : \text{trans-}\beta = 58 : 42$  (in the absence of CO it is equal to 18 : 82). The observed increases of  $\alpha$ -product formation demonstrate that by changing the atmosphere in which reaction is performed, the nature of platinum hydrochloric acid system can be modified simply and it plays a significant role on the direction of the reaction.<sup>8</sup>

The reaction between phenylacetylene and transition metal-substituted silane ( $\eta^5\text{-C}_5\text{H}_5$ ) $\text{Fe}(\text{CO})_2\text{SiPh}_2\text{H}$  in the presence of platinum hydrochloric acid resulted in significantly greater amounts of the  $\alpha$ -addition product than that normally found when this catalyst is used ( $\alpha : \beta = 80 : 20$ )<sup>9</sup>:



During hydride addition reactions of trichlorosilane and methylchlorosilane to phenylacetylene in the presence of Pt/C and  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , the obtained silyl-substituted styrene can attach to second molecule of hydride silane<sup>2</sup>:



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## EXPERIMENTAL

The starting materials for the synthesis of methylsiloxane oligomers with reactionable double-bonded phenethenyl substituted groups in the side chain were  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane and phenylacetylene.

The initial  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane with the degree of polymerization  $n \approx 35$  and phenylacetylene was received from Fluka (Sigma-Aldrich). The organic solvents were cleaned by drying and distillation.

The IR spectra of all samples were obtained with an UR-20 spectrophotometer, from KBr pellets, while the  $^1\text{H}$  NMR spectra was obtained with a Perkin-Elmer instrument at an operating frequency of 250 MHz. All spectra were obtained with the use of  $\text{CDCl}_3$  as solvent and an internal standard. The Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine TGA and the thermal transition temperatures ( $T_g$ ) were read at the maximum of the endothermic or exothermic peaks. Heating and cooling scanning rates were  $10^\circ\text{C}/\text{min}$ .

Using Waters Model 6000A chromatograph with an R 401 differential refractometer detector, gel-permeation chromatography investigation was carried out. The column set comprised  $10^3$  and  $10^4 \text{ \AA}$  Ultrastayragel columns. Sample concentration was  $\sim 3\%$  by weight in toluene and typical injection volume for the siloxane was  $5 \mu\text{L}$ . Standardization of the GPC was accomplished by using styrene or polydimethylsiloxane standards with the known molecular weight.

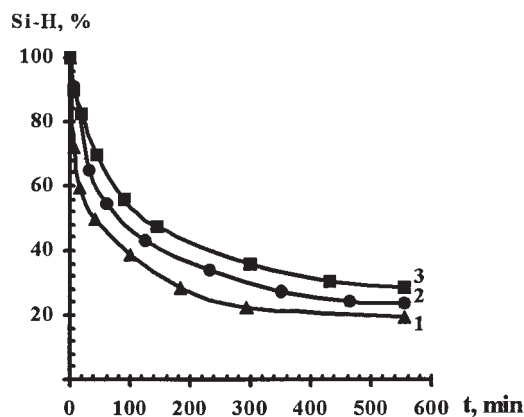
Wide-angle X-ray diffractograms were obtained with a DRON-2 instrument.  $\text{Cu K}\alpha$  was measured without a filter, the angular velocity of the motor was  $\omega \approx 2^\circ/\text{min}$ .

### Hydrosilylation reaction of $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to phenylacetylene

Hydrosilylation reaction was carried out in a three-necked flask equipped with a tube for catalyst inlet, a reflux condenser, and an inert gas carrier tube. The reaction products 1.4699 g (0.7491 mmole)  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane and 2.2958 g (22.473 mmole) phenylacetylene 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 ( $5\text{--}9 \times 10^{-5} \text{ g}/1.0 \text{ g}$  of starting substance), was introduced. After the reaction was over, the solvent was eliminated.

## RESULTS AND DISCUSSION

From the literature, it is known that insertion of various heteroatom or cyclic fragments in the linear dim-



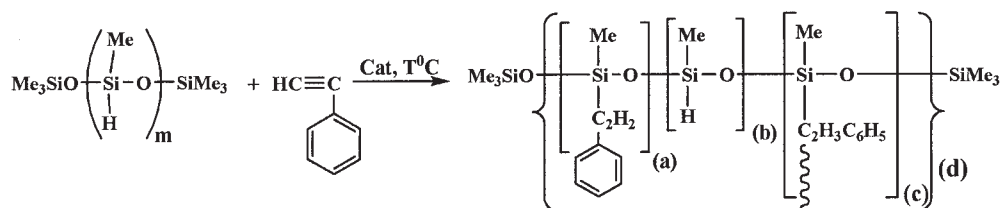
**Figure 1** Dependence of changes of concentration of active (Si—H group) on the time, upon hydrosilylation reaction of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to phenylacetylene, where curve 1 represents the values obtained at  $60^\circ\text{C}$ , curve 2 represents the values obtained at  $50^\circ\text{C}$ , and curve 3 represents the values obtained at  $40^\circ\text{C}$ .

ethylsiloxane backbone breaks the spiral structure of polydimethylsiloxane chain and changes the physical-chemical indices and thermal-oxidative stability of copolymers.<sup>10</sup> The insertion of more rigid phenyl fragments in the main polydimethylsiloxane (PDMS) backbone hinders the depolymerization processes of polymeric chain, which is accompanied by release of cyclic  $\text{D}_n$  type dimethylcyclosiloxanes  $[\text{Me}_2\text{SiO}]_n$ . Such types of polymers are characterized by higher thermal-oxidative stability. Increased thermal-oxidative stability of copolymers may be explained by the presence of phenyl groups that are highly resistant to oxidation, and with their inhibiting effect on oxidation of methyl groups.<sup>11,12</sup>

For synthesis of new siliconorganic oligomers with double-bonded phenethenyl groups in the side chain, the hydrosilylation reaction of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydridesiloxane to phenylacetylene, in the presence of catalyst (0.1M solution of platinum hydrochloric acid in tetrahydrofuran), at 1 : 35 ratio of initial compounds has been investigated.

Preliminary heating of initial compounds in the temperature range of  $40\text{--}60^\circ\text{C}$  in the presence of catalyst showed that, in these conditions, polymerization of phenylacetylene, or other changes due to break in siloxane backbone, or elimination of methane from methylhydridesiloxane do not take place. Besides, there are no changes in the NMR and IR spectra of initial compounds. By gas-liquid chromatography it was established that the polymerization of phenylacetylene does not proceed in this condition.

During the hydrosilylation reaction, the decrease of active  $\equiv \text{Si-H}$  groups on time was observed. The hydrosilylation reaction was investigated in dry toluene solution ( $C \approx 6.8 \times 10^{-2} \text{ mol/L}$ ). It was established that all active Si—H groups do not take part in



**Scheme 1.** Hydrosilylation reactions of  $\alpha,\omega$ -bis(trimethylsilyloxy)methylhydridesiloxane to phenylacetylene.

hydrosilylation reaction. From Figure 1 one can observe dependence of changes of active  $\equiv\text{Si}-\text{H}$  groups on time during hydrosilylation reaction of  $\alpha,\omega$ -bis(trimethylsilyloxy)methylhydridesiloxane to phenylacetylene.

From Figure 1 it is evident that at  $40^\circ\text{C}$  hydrosilylation reaction proceeds with  $\sim 80\%$  conversion of active  $\equiv\text{Si}-\text{H}$  groups, whereas at  $60^\circ\text{C}$  hydrosilylation reaction proceeds with  $\sim 92\%$  conversion. Consequently, with the rise of temperature, the depth of hydrosilylation reaction increases.

So, the hydrosilylation reaction of  $\alpha,\omega$ -bis(trimethylsilyloxy)methylhydridesiloxane to phenylacetylene in general proceeds according to the Scheme 1 in which [(a)+(b)+(c)](d) =  $m \approx 35$ ;  $60^\circ\text{C}-\text{I}$ ,  $50^\circ\text{C}-\text{I}^1$ ,  $40^\circ\text{C}-\text{I}^2$ .

Hydrosilylation proceeds rapidly in the first 1 h, and then the reactions proceed with low rate. Synthesized oligomers are orange liquids, well soluble in ordinary aromatic type organic solvents with  $\eta_{\text{sp}} \approx 0.07-0.08$ . Structure and composition of oligomers were proved by elementary analysis, determination of molecular masses, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data. Some physical-chemical properties of synthesized oligomers are presented in Table I.

After elimination of the solvent NMR and IR spectra investigations were carried out.

In the IR spectra of oligomers one can observe absorption bands at  $1025\text{ cm}^{-1}$ , characteristic of asymmetric valence oscillation of linear  $\text{Si}-\text{O}-\text{Si}$  bonds. In the regions  $840$ ,  $1410$ , and  $1275\text{ cm}^{-1}$ , one can observe absorption bands characteristic for  $-\text{SiMe}_3$ ,  $\equiv\text{Si}-\text{CH}=\text{C}$ , and  $\equiv\text{Si}-\text{Me}$  bonds, respectively. In IR spectra there was no signal at  $2160\text{ cm}^{-1}$  characteristic for  $\equiv\text{Si}-\text{H}$  bonds, which indicate that during elimination of solvent full intermolecular hydrosilylation takes place and branched systems were obtained.

In the  $^1\text{H}$  NMR spectra of oligomer I (Fig. 2), one can observe singlet signals for protons in  $\equiv\text{Si}-\text{Me}$ ,  $-\text{SiMe}_3$ , and Me group with chemical shift in the range  $\delta \approx 0.05-0.44$  ppm. In the spectra one can observe signal for protons of methine group in the fragment  $\equiv\text{Si}-\text{CH}=\text{C}$ , with center of chemical shift  $\delta \approx 5.8$  ppm, and signal with center of chemical shift  $\delta \approx 6.2$  ppm which corresponds to protons of methine group in  $\text{Ph}-\text{CH}=\text{C}$  fragment. In the spectra one can observe multiplet signal characteristic for protons of phenyl group in the range  $\delta \approx 6.7-7.4$  ppm. One can also observe two signals with center of chemical shifts at  $1.22$  ppm and  $1.57$  ppm, which corresponds to methylene protons; triplet signal with center of chemical shift at  $0.82$  ppm corresponds to protons in methine fragment. Formation of these complementary signals may be explained because of branching processes after elimination of solvent.

$^{13}\text{C}$  NMR spectra of oligomer I is in complete conformity with  $^1\text{H}$  NMR spectral data. In the spectra one can observe double-tuned signals for carbon-silicon fragment with chemical shift  $\delta \approx 125.3$  ppm and for  $\text{C}-\text{C}_{\text{ar}}$  double-tuned signals with chemical shift  $\delta \approx 125.5$  ppm. It shows that there are two isomeric products *cis*- and *trans*- $\beta$ -vinylsilane. In the spectra one can observe resonance signal for carbon nucleus of aromatic fragment with chemical shift  $\delta \approx 126.1-129.0$  ppm.

Figure 3 shows dependence of reverse concentration on time during the hydrosilylation reaction of methylhydridesiloxane to phenylacetylene. One can see that at the initial stages the hydrosilylation reaction is of second order.

The reaction rate constants of hydrosilylation reactions of methylhydridesiloxane to phenylacetylene at various temperatures were determined, which values are:  $k_{40^\circ\text{C}} \approx 0.9457 \times 10^{-2}$ ,  $k_{50^\circ\text{C}} \approx 1.4998$  and  $k_{60^\circ\text{C}} \approx$

**TABLE I**  
Some Physical-Chemical Properties of Synthesized Oligomers

No oligomers	Yield (%)	$\eta_{\text{sp}}$ in 1% toluene solution at $25^\circ\text{C}$	Reaction temperature ( $^\circ\text{C}$ )	Conversion of active $\equiv\text{Si}-\text{H}\%$ group	$T_g$ ( $^\circ\text{C}$ )	10% mass losses ( $^\circ\text{C}$ )	$M_w \times 10^{-4}$
I	92	0.08	60	83	-45	350	4.14
I <sup>1</sup>	91	0.07	50	76	—	—	—
I <sup>2</sup>	91	0.07	40	71	—	—	—

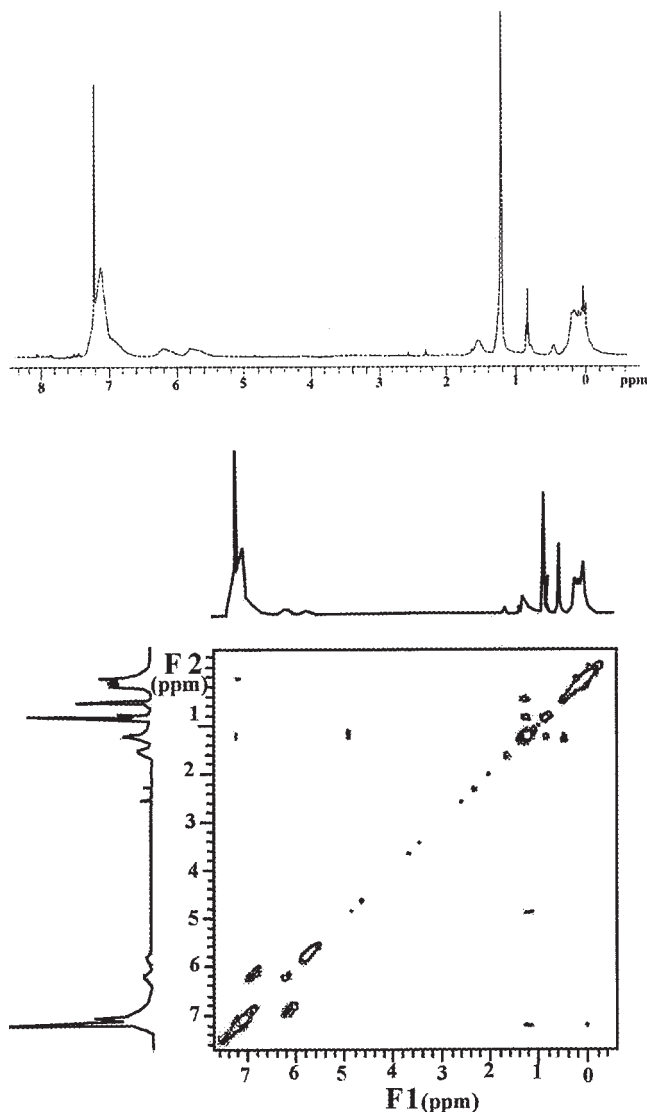


Figure 2 The  $^1\text{H}$  NMR and COZY spectra of oligomer I.

2.3571 1/(mol.s). The reaction temperature coefficient is equal to  $\gamma \approx 1.6$ .

From the dependence of hydrosilylation reaction rate constants' logarithm on the reverse temperature, the activation energy of hydrosilylation reaction was calculated, which is equal to:  $E_{\text{act}} \approx 54.6$  kJ/mol.

Figure 4 shows the molecular weight distribution of oligomer I, from which it is evident that oligomer I has trimodal molecular weight distribution. Its molecular weight is equal to:  $\bar{M}_n \approx 6.94 \times 10^3$ ,  $\bar{M}_w \approx 4.14 \times 10^4$ , and polydispersity  $D \approx 5.97$ .

As it is obvious the average molecular masses of synthesized oligomers several times exceed theoretical values of calculated molecular masses in case of full hydrosilylation. It indicates that during hydrosilylation reaction branching process also takes place according to the general scheme:

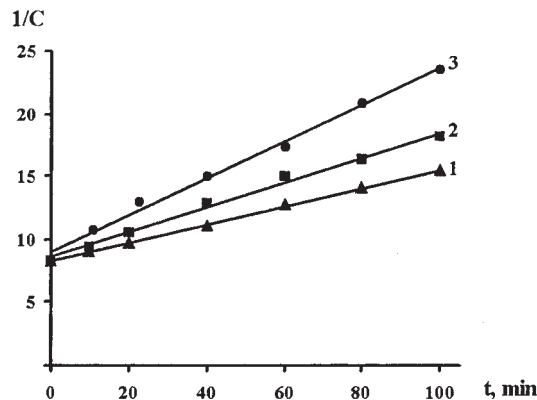
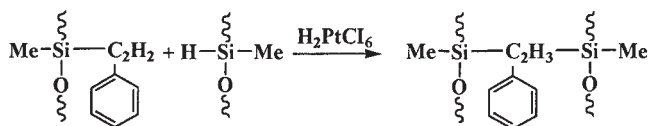


Figure 3 Dependence of inverse concentration on time during the hydrosilylation reaction of methylhydridesiloxane to phenylacetylene, where curve 1 represents the values obtained at  $60^\circ\text{C}$ , curve 2 represents the values obtained at  $50^\circ\text{C}$ , and curve 3 represents the values obtained at  $40^\circ\text{C}$ .



Increased molecular masses proved that during intermolecular hydrosilylation reaction according to Markovnikov and Farmer rule, branched oligomers are obtained. Obtaining of branching systems may also proceed with participation of residual  $\equiv\text{Si}-\text{H}$  groups in intermolecular crosslinking reactions with obtaining of  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  and  $\equiv\text{Si}-\text{Si}\equiv$  bonds, which were discussed earlier.<sup>13,14</sup>

Differential scanning calorimetric (DSC) investigation for synthesized oligomers has been carried out (Fig. 5). As it is seen from DSC curves for oligomer I only one endothermic peak, with one temperature transition, which corresponds to glass transition temperature  $T_g \approx -45^\circ\text{C}$  is observed.

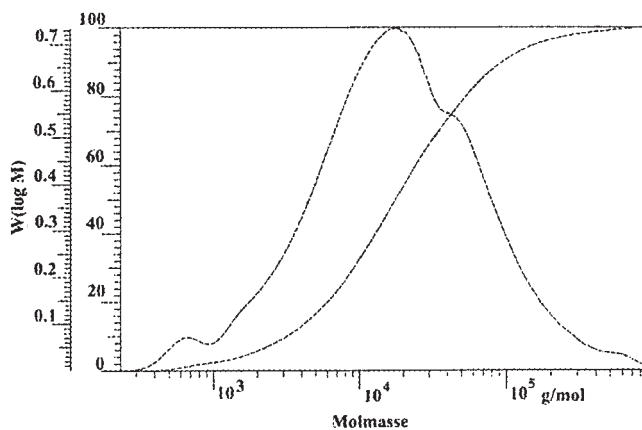
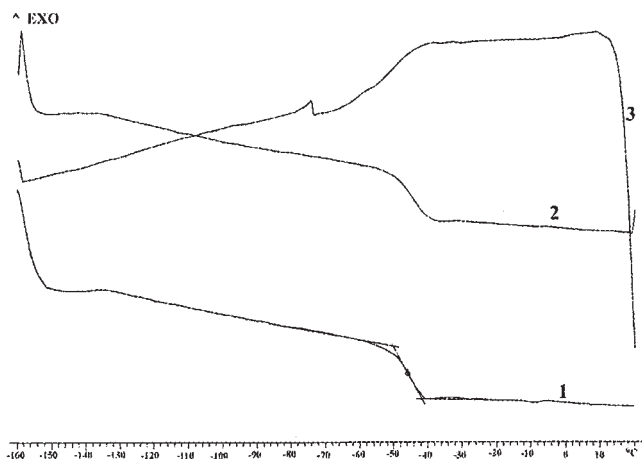


Figure 4 Gel-permeation chromatographic curves of oligomer I.



**Figure 5** DSC curves of oligomer I. Curves 1 and 2 correspond to first and second heating scanning and curve 3 corresponds to cooling scanning.

Thermogravimetric investigations of synthesized oligomers were carried out. For oligomers, the mass losses at 250°C temperature are not observed, whereas unblocked polydimethylsiloxane polymer is completely destroyed in the 270–280°C temperature range.<sup>15</sup> Mass losses (10%) are observed at ~380°C and the main destruction process proceeds from 400°C. It was shown that by insertion of aryl fragments in dimethylsiloxane chain thermal-oxidative stability of oligomers increased.

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