

# Formation of Polymethylsiloxanes with Alkyl Side Groups

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**ABSTRACT:** Hydrosilylation of  $\alpha,\omega$ -bis(trimethylsiloxy)-methylhydrosiloxane to alkenes in the presence of a catalyst was performed at several temperatures (30–70°C). Comb-type methylsiloxane oligomers with various alkyl substituted groups in the side chains have been obtained. Not all active  $\equiv\text{Si}-\text{H}$  groups participate in the reaction. The reaction order, activation energies, and rate constants have been determined. The synthesized oligomers were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$  COSY NMR, and FTIR spectroscopy. Calculations using the quantum-chemical semiempirical AM1 method for modeling reaction between methyltrimethoxysilane [ $\text{Me}(\text{MeO})_2\text{SiH}$ ] and hexene-1 were performed to evaluate

possible reaction paths. For all initial, intermediate, and final products, enthalpies of formation as a function of the distance between  $\equiv\text{C}-\text{Si}\equiv$  bonds are calculated. The hydride addition is energetically more favorable according to the anti-Markovnikov rule than according to the Markovnikov rule. Comb-type oligomers were characterized by gel-permeation chromatography, differential scanning calorimetry, thermogravimetry, and wide-angle X-ray diffractometry. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1176–1183, 2007

**Key words:** polysiloxanes; hydrosilylation; calculations; NMR; gel-permeation chromatography

## INTRODUCTION

There is an increasing interest in polymers with inorganic backbones due to some advantages they have over carbon-chain polymers.<sup>1,2</sup> Polysiloxanes attract the widest interest among the inorganic backbone polymers. The reason lies in properties of polysiloxanes such as strong heat resistance, elastomeric behavior, biocompatibility, thermal-, UV- and oxidative stabilities, low surface energy, good weatherability, low melting points and glass transition temperatures, convenient rheological properties, and outstanding electrical properties.<sup>3</sup>

The properties of organosilicon polymers depend on the structure of macromolecular chains and on the nature of organic groups surrounding the silicon atom.<sup>4</sup> In comb-type copolymers we have organic substituent groups of different size and nature bonded to the methylsiloxane hydrophobic matrix. A wide range of variation of these substituent groups is possible. Some siliconorganic copolymers contain mesogenic groups and exhibit liquid-crystalline properties.<sup>5–7</sup> In polydialkylsiloxanes, independently

of the main chain, one observes the formation of mesomorphic states mainly in the presence of mesogenic alkyl substituents ( $R = \text{C}_n\text{H}_{2n+1}$ ,  $n \geq 2$ ).

For synthesis of comb-type polymers there are two main options. One is polymerization of unsaturated or cyclic monomers, in which side fragments with mesogenic properties already exist in initial monomer molecules. In the second option, one attaches new units to a preexisting matrix. We have decided to follow the second route and to obtain new comb-type organosilicon oligomers by insertion of various side groups into methylhydrosiloxane oligomers. Our approach has certain advantages. We have taken a commercially available polymethylhydrosiloxane. The catalyst we have used is one of the cheapest available. Potential applications of the materials we have obtained as stationary phases for gas-liquid chromatography deserved to be explored. As classified by one of us<sup>8</sup> and amplified by Hess,<sup>9</sup> there exists a variety of polymer liquid crystal (PLC) combs, including palisade combs, disc combs, and more. Formation of LC phases by our synthesis products also deserved exploration.

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## EXPERIMENTAL

### Materials and techniques

The starting materials for the synthesis of comb-type methylalkylsiloxane oligomers with various length of

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TABLE I  
Some Physical–Chemical Properties of Synthesized Oligomers

Symbol	Yield (%)	$\eta_{sp}$	Reaction temperature (°C)	% Conversion of active $\equiv\text{Si}-\text{H}$ groups	$d_1$ (nm)	$T_g$ (°C)	Temperatures (°C) for 5% mass losses	$\overline{M}_w$ ( $10^{-4}$ )
I	93	0.07	50	94	1.141	-112	270–300	2.86 (3.96) <sup>a</sup>
I <sup>1</sup>	92	0.06	40	86	–	–	–	–
I <sup>2</sup>	92	0.06	30	82	–	–	–	–
II	92	0.07	60	93	1.255	–	290–315	–
III	91	0.09	60	89	1.361	–	–	2.95 (2.99)
III <sup>1</sup>	90	0.08	50	79	–	–	–	–
III <sup>2</sup>	90	0.08	40	66	–	–	–	–
IV	88	0.09	70	86	1.607	-42	350–370	–
V	86	0.09	70	82	1.864	–	–	4.50 (3.88)
VI	85	0.10	70	78	2.054	+44	370–390	2.59 (1.88)

<sup>a</sup> Values within parentheses indicate polydispersity indices.

alkyl substituted groups in the side chain were  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydrosiloxane, *n*-hexene-1, *n*-heptene-1, *n*-octene-1, *n*-decene-1, *n*-dodecene-1, and *n*-octadecene.

The initial  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydrosiloxane had the degree of polymerization  $n \approx 35$ ; alkenes with normal structure: hexene-1, heptene-1, octene-1, decene-1, dodecene-1, and octadecene-1 were obtained from Aldrich (Steinheim, Germany) and used as received. The organic solvents were cleaned by drying and distillation.

FTIR spectra were obtained on a Nicolet Nexus 470 machine with MCTB detector. <sup>1</sup>H, <sup>1</sup>H COSY, and <sup>13</sup>C-NMR spectra were recorded on a ARX400 Bruker NMR spectrometer at 400 MHz operating frequency, using CDCl<sub>3</sub> as the solvent and an internal standard.

Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA-7 machine at the heating rate of 10 K min<sup>-1</sup>. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC-7 apparatus. Thermal transitions including glass transition temperatures  $T_g$  were taken as the middle point of the falls.<sup>10</sup> The heating and cooling scanning rates were 10 K min<sup>-1</sup>. Transitions due to formation of liquid crystalline phases was not observed, apparently no LC phases are formed in our systems.

Gel-permeation chromatography (GPC) was performed using a Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10<sup>2</sup> and 10<sup>3</sup> nm Ultrastyrigel columns. The sample concentrations were 3% by weight in toluene; a typical injection volume for the siloxane was 5  $\mu\text{L}$ . Standardization of the GPC was accomplished with styrene or polydimethylsiloxane standards with known molecular masses, a typical procedure. The chromatograph provides several average molecular masses ( $\overline{M}_n$ ,  $\overline{M}_w$ ,  $\overline{M}_z$ ,  $\overline{M}_v$ ) and thus also the polydispersity indices (listed in parentheses in the last column of Table I).

Wide-angle X-ray diffractograms were taken on a DRON-2 (Burevestnik, St Petersburg, Russia) instrument. A Cu K $\alpha$  was measured without a filter; the angular velocity of the motor was  $\omega \approx 2 \text{ deg min}^{-1}$ .

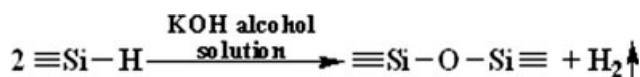
#### Hydrosilylation reaction of $\alpha,\omega$ -bis(trimethylsiloxy)methylhydrosiloxane to *n*-hexene-1

Hydrosilylation was carried out in a two-necked flask equipped with a magnetic stirrer, a tube for catalyst inlet, and a reflux condenser.

The reaction products 0.99 g (0.44 mmol)  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydrosiloxane and 1.28 g (0.0154 mol) *n*-hexene-1 and 5.4 mL dry toluene were placed into the flask and then into an oil bath until a constant temperature was reached in argon atmosphere. Then the catalyst 0.1M solution of platinum hydrochloric acid in tetrahydrofuran ( $5 \times 10^{-5}$  to  $9 \times 10^{-5}$  g per 1.0 g of starting substance) was introduced. After the reaction completion, the solvent was partially eliminated, the reaction product was precipitated from toluene solution by *n*-hexane, and 2.1 g (93%) oligomer I was obtained. The hydrosilylation reaction with other alkenes was carried out by the aforementioned reaction, using the same catalyst, i.e., H<sub>2</sub>PtCl<sub>6</sub> (0.1M solution in tetrahydrofuran).

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

We calculate the content of active  $\equiv\text{Si}-\text{H}$  groups in oligomers according to the well-known method on the basis of the following reaction (Scheme 1).<sup>11</sup>



**Scheme 1** Basis reaction for determination of the content of active  $\equiv\text{Si}-\text{H}$  groups.



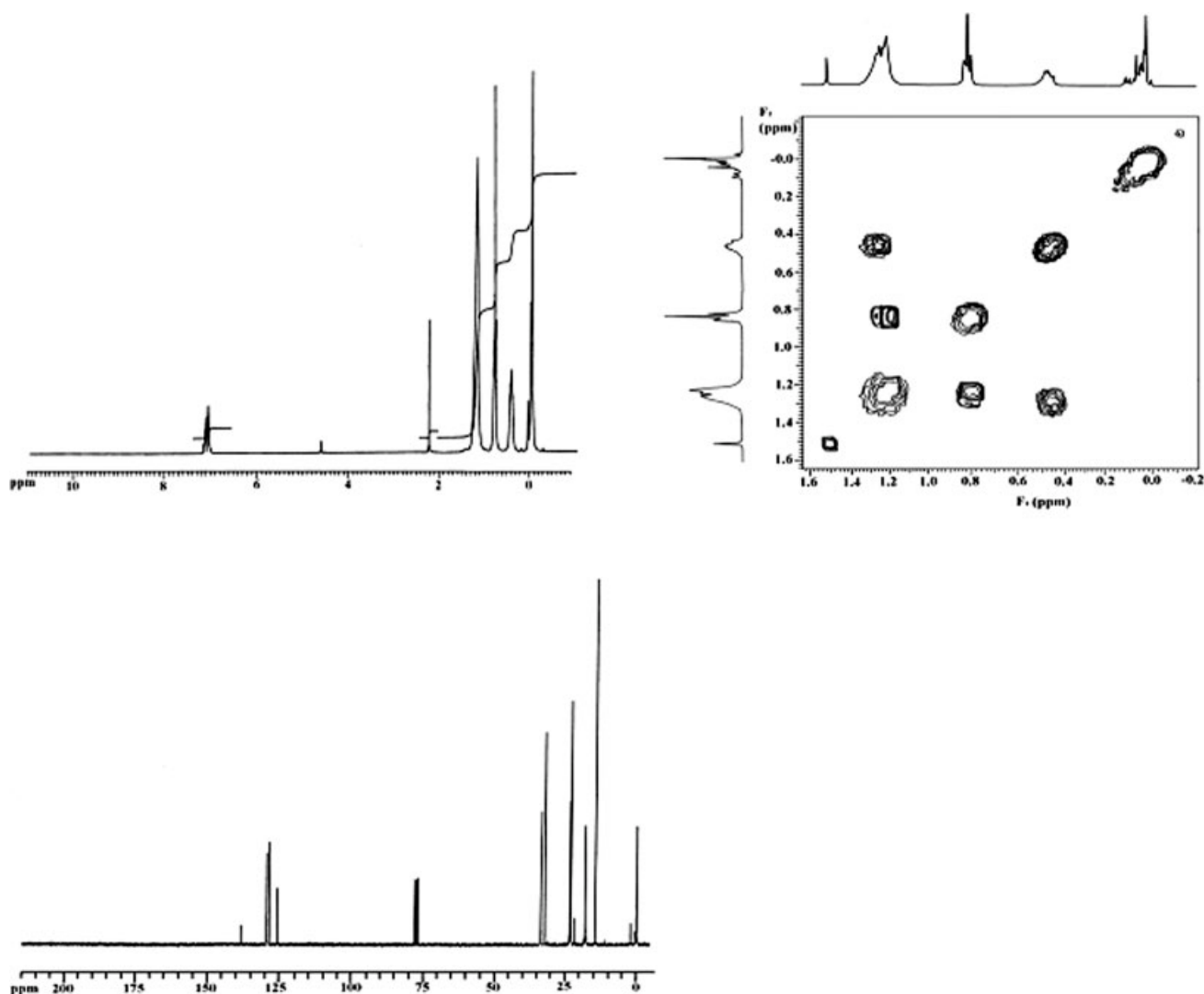


Figure 3  $^1\text{H}$ ,  $^1\text{H}$  COSY, and  $^{13}\text{C}$  NMR spectra of oligomer I.

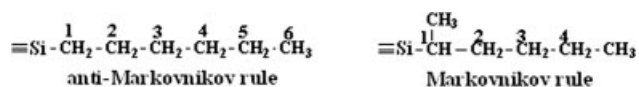
$1085\text{ cm}^{-1}$ . In the  $770$  and  $1259\text{ cm}^{-1}$  regions, we see the absorption bands characteristic for Si—C and Si—CH<sub>3</sub>. With an increase of the length of side groups, intensity of symmetric valence oscillations in the region  $2850$ – $2955\text{ cm}^{-1}$ , characteristic for CH<sub>2</sub> groups, increases as it should. Further, we observe an absorption band around  $2165\text{ cm}^{-1}$  corresponding to unreacted Si—H bonds. We find a signal with low intensity around  $1187\text{ cm}^{-1}$  characteristic for silsesquioxane bonds (SiO<sub>3/2</sub>); side reactions due to cross-linking are clearly insignificant. The signal in question is absent in the FTIR spectra of initial  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydrosiloxane.

In Figure 3 we show  $^1\text{H}$ ,  $^1\text{H}$  COSY, and  $^{13}\text{C}$ -NMR spectra of oligomer I.

In Scheme 4 we show structural formulas of the fragments in hydrosilylation products of PMHS with hexene-1. In Tables II and III we present NMR spectral data for oligomer I.

Given the two rules enunciated earlier, we infer that the reaction proceeds more according to the anti-Markovnikov rule but also partially according to the Markovnikov rule. The ratio of the fragments obtained from the anti-Markovnikov and Markovnikov rules is equal to 5.4 : 1. We calculate the ratio of the fragments from comparison of  $\equiv\text{Si}-\text{CH}_2$  and  $\equiv\text{Si}-\text{Me}$  signal intensities in view of active  $\equiv\text{Si}-\text{H}$  group conversion. It is not possible to calculate the ratio from Si—CH signals because of overlapping with other signals.

In  $^1\text{H}$ -NMR of oligomers I–VI we have signals with the same chemical shifts but with different intensities.



Scheme 4 Structural formulas of the fragments in hydrosilylation products of PMHS with hexene-1.



TABLE II  
 $^1\text{H}$  NMR  $\delta$  (ppm) of Oligomer I

Si-CH <sub>3</sub>	0.1
Si(CH <sub>3</sub> ) <sub>3</sub>	0.2
Si-CH <sub>2</sub>	0.48
C <sub>2-3</sub> H <sub>2</sub>	0.8–0.95
C <sub>4-5</sub> H <sub>2</sub>	1.1–1.2
CH <sub>2</sub> CH <sub>3</sub>	0.85
Si-CH	1.1–1.3
CHCH <sub>3</sub>	0.8

As in the case of oligomer I, we calculate the approximate ratio of the fragments obtained from the anti-Markovnikov and Markovnikov rules; the results are presented in Table IV.

With increase of the length of substituted alkyl groups, the reaction goes predominantly according to the anti-Markovnikov rule.

### QUANTUM-CHEMICAL AND KINETIC CALCULATIONS

Semiempirical quantum methods we have used are simplified versions of the Hartree-Fock self-consistent field approach using empirical corrections derived from experimental data. These methods are usually referred to through acronyms encoding some of the underlying theoretical assumptions. We apply one of the most frequently used AM1 methods. It is based on the neglect of differential diatomic overlap (NDDO) integral approximation. This approach belongs to the class of zero differential overlap (ZDO) methods, in which all two-electron integrals involving two-center charge distributions are neglected. A number of additional approximations are made to speed up calculations and a number of parameterized corrections are made to correct for the approximations in the quantum mechanical model. For AM1 the parameterization is performed so that we obtain enthalpies of formation  $H^{\text{form}}$  instead of total enthalpies<sup>13</sup> as a function of the distance  $R_{\text{C-Si}}$ . The calculations provide us also with  $P_{x-y}$  values which represent bond orders.

We have performed calculations using a semiempirical AM1 method for modeling reaction between methyltrimethoxysilane [Me(MeO)<sub>2</sub>SiH] and hexene-1

TABLE III  
 $^{13}\text{C}$  NMR  $\delta$  (ppm) of Oligomer I

Si-CH <sub>2</sub>	17.79
C <sub>2</sub> H <sub>2</sub>	17.99
C <sub>3</sub> H <sub>2</sub>	33.53
C <sub>4</sub> H <sub>2</sub>	32.06
C <sub>5</sub> H <sub>2</sub>	23.4
CH <sub>2</sub> CH <sub>3</sub>	14
Si-CH	18.08
CHCH <sub>3</sub>	2.15

TABLE IV  
 Ratio of the Fragments Obtained from the Anti-Markovnikov and Markovnikov Rules

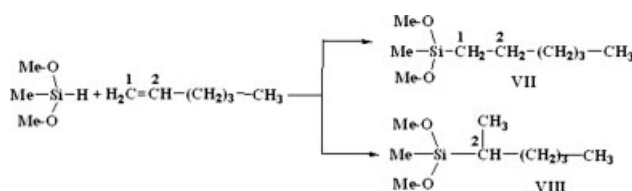
Oligomer	Anti-Markovnikov / Markovnikov
I	5.4/1
II	6.5/1
III	7.8/1
IV	8.3/1
V	8.5/1
VI	9.2/1

for full characterization of hydride addition of polymethylhydrosiloxane to hexene-1, using software Chem3D Ultra 9.0 from Cambridge Soft (Cambridge, UK). Such calculations for polymethylhydrosiloxane and hexene-1 are not doable since the software does not produce reliable results for systems with more than 100 atoms. Necessarily, numerical values for the model reaction will be different than for the polymers studied experimentally but will provide better understanding of the experimental results.<sup>14</sup>

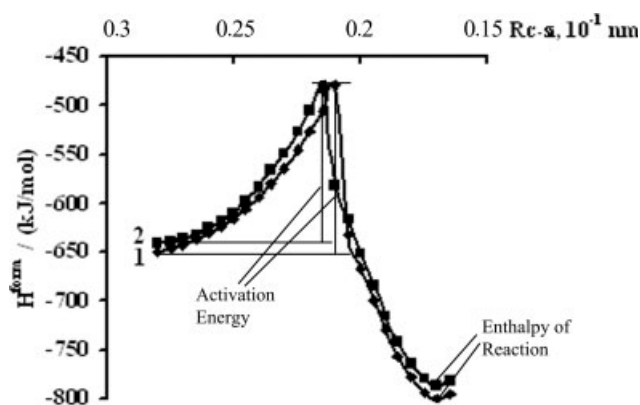
We consider the hydrosilylation of [Me(MeO)<sub>2</sub>SiH] with hexene-1 in view of the anti-Markovnikov and Markovnikov rules. The model reactions proceed with formation of compounds VII and VIII (Scheme 5):

The distance between the double bonded carbon atom C<sub>1-2</sub> and silicon was assumed 0.1 nm longer than the bond length expected in the product. The distance  $R_{\text{C-Si}}$  between the atom of silicon and the double bonded carbon atom C<sub>1-2</sub> was assumed = 0.005 nm. Enthalpies of formation  $H^{\text{form}}$  calculated from AM1 as a function of the distance  $R_{\text{C-Si}}$  is presented in Figure 4.

We see that  $H^{\text{form}}$  monotonously decreases with decreasing distance while strengthening of newly formed bonds takes place. The calculated enthalpy of formation of the hydrosilylation product  $H^{\text{form}} = -800 \text{ kJ mol}^{-1}$  agrees with  $H^{\text{form}} = -807 \text{ kJ mol}^{-1}$  of compound VIII obtained by hydride addition of methyltrimethoxysilane to hexene-1, according to the anti-Markovnikov rule. We have calculated the activation energy  $U_{\text{act}} = 161.9 \text{ kJ mol}^{-1}$  for the modeling reaction proceeding by anti-Markovnikov rule from the difference of the maxima and the initial points in Figure 4. Also the calculated  $H^{\text{form}} = -792.03 \text{ kJ mol}^{-1}$  agrees with



Scheme 5 Model reaction of hydrosilylation of [Me(MeO)<sub>2</sub>SiH] with hexene-1.

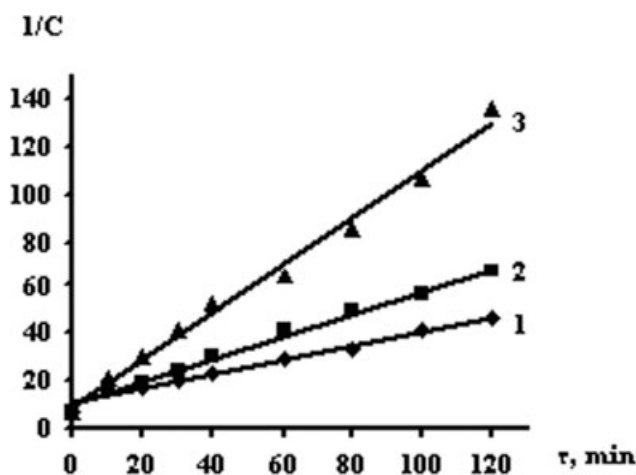


**Figure 4** Enthalpy of formation  $H^{\text{form}}$  as a function of the distance  $R_{\text{C-Si}}$  between silicon and carbon atoms from modeling of reaction of methyltrimethoxysilane toward hexene-1, according to the anti-Markovnikov (1) and Markovnikov rules (2).

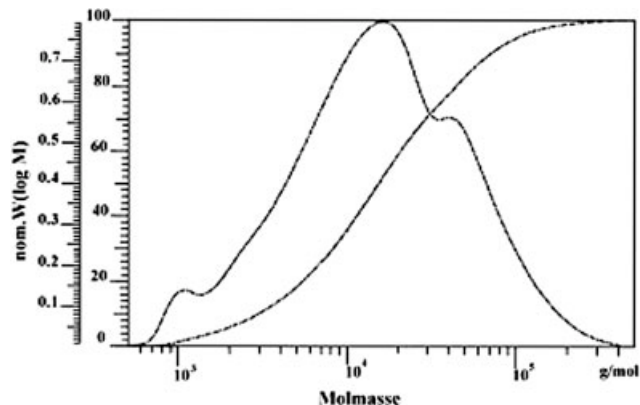
$H^{\text{form}} = -785.79 \text{ kJ mol}^{-1}$  of compound VIII obtained by hydride addition of methyltrimethoxysilane to hexene-1 according to the Markovnikov rule. We obtain the activation energy  $U_{\text{act}} = 158.9 \text{ kJ mol}^{-1}$  for the modeling reaction using the same method. As expected, there are large difference between the experimental values for our polymers and calculation results for model monomer compounds.

Compare now  $H^{\text{form}}$  values for compounds VII and VIII taking also into account Figure 4. Clearly hydrosilylation reaction of methyltrimethoxysilane to hexene-1 is energetically more favorable according to the anti-Markovnikov rule behind to Markovnikov rule. This result is in agreement with NMR spectral data.

Figure 5 shows dependence of the reciprocal concentration of  $\equiv\text{Si-H}$  groups on time during the hydrosilylation reaction. We see that initially the reac-



**Figure 5** Dependence of reciprocal concentration of  $\equiv\text{Si-H}$  groups on time during the hydrosilylation reaction of methylhydridesiloxane to hexene-1. Curve 1 pertains to  $50^\circ\text{C}$ , curve 2 to  $40^\circ\text{C}$ , and curve 3 to  $30^\circ\text{C}$ .



**Figure 6** Gel-permeation chromatographic curves of oligomer I.

tion is of the second order. The procedure provides us also with true rate constants.

We have calculated the reaction rate constants of hydrosilylation reactions of methylhydrosiloxane to hexene-1 and octene-1 for several temperatures. The results are:  $k_{30^\circ\text{C}} \approx 0.223$ ,  $k_{40^\circ\text{C}} \approx 0.395$  and  $k_{50^\circ\text{C}} \approx 0.737 \text{ mol L}^{-1} \text{ s}^{-1}$  for hexene-1;  $k_{40^\circ\text{C}} \approx 0.134$ ,  $k_{50^\circ\text{C}} \approx 0.237$  and  $k_{60^\circ\text{C}} \approx 0.404 \text{ mol L}^{-1} \text{ s}^{-1}$  for octene-1.

We have calculated the activation energies for the reactions, using logarithmic reaction rate constants as functions of the reciprocal temperature. The results are:  $U_{\text{act}} \approx 46.3 \text{ kJ mol}^{-1}$  for hexene-1 and  $U_{\text{act}} \approx 44.7 \text{ kJ mol}^{-1}$  for octene-1.

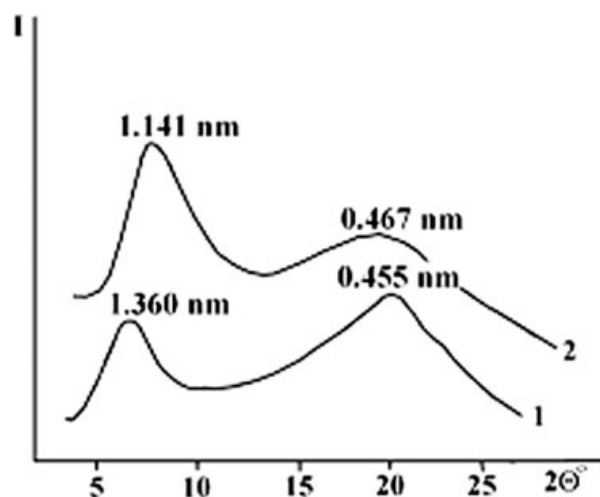
## GPC RESULTS

The synthesized oligomers were studied by GPC. Figure 6 shows the molecular weight distribution of oligomer I. A trimodal curve is seen. We find the number average molecular mass  $\bar{M}_n \approx 7.23 \times 10^3$  and the weight average molecular mass  $\bar{M}_w \approx 2.86 \times 10^4$ . Thus, the polydispersity index is equal to 3.96.

The average molecular weights of synthesized oligomers exceed several times the theoretical values calculated for the full hydrosilylation. This indicates that branching processes take place during the reaction. The difference in appearance and degree of crosslinking can be attributed to the effectiveness of the different Pt-species of  $\text{H}_2\text{PtCl}_6$ , which cannot be separated from oligomers after reaction. Pt is partially in the form of Pt(II). It reacts with the  $\text{Si-H}$  group of the PMHS backbone with elimination of hydrogen and producing Pt metal. This fact leads us to suggest that crosslinking occurs according to the following scheme (Scheme 6)<sup>15,16</sup>:



**Scheme 6** Suggested scheme of the crosslinking during hydrosilylation of PMHS with alkenes.



**Figure 7** X-ray patterns for methylsiloxane comb-type PLC oligomers. Curve 1 corresponds to oligomer III and curve 2 to oligomer I.

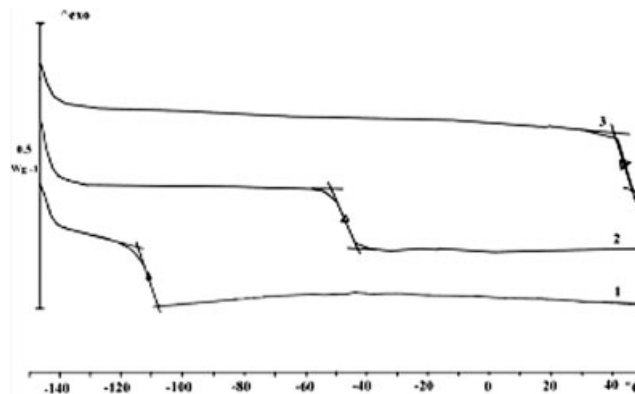
As mentioned earlier, the FTIR spectrum of oligomer I (Fig. 2) shows formation of silsesquioxane bonds ( $\text{SiO}_{3/2}$ ) but to a low extent only.

#### WIDE ANGLE X-RAY DIFFRACTOMETRY RESULTS

We have determined for our oligomers wide-angle X-ray scattering (WAXS). Figure 7 shows that the oligomers are amorphous one-phase systems. Diffraction patterns display two maxima. The main one on the left side corresponds to the maximum of the interchain distance  $d_1$  while the second corresponds to  $d_2$  which characterizes both intramolecular and interchain interactions.<sup>17</sup> With an increase of the length of alkyl side groups, the interchain distance  $d_1$  increases from 1.141 nm (oligomer I) to 2.054 nm (oligomer VI). Platé and Shibaev report values of interchain distances for comb-type poly-1-alkylethylene PLCs.<sup>18</sup> Our  $d_1$  values are similar.

#### CALORIMETRIC RESULTS: DSC AND TGA

DSC and TGA techniques have been described by Menard.<sup>10</sup> We have performed DSC scans from  $-170^\circ\text{C}$  to  $+70^\circ\text{C}$ ; we show only the eventful parts of the diagrams. There were no significant differences between the first and second heating runs. We display in Figure 8 DSC results from second runs for oligomers I, IV, and VI. There are only single endothermic peaks which correspond to the glass transitions (see Table I). Gurgenidze has attached oxyhexyl groups to the methylsiloxane matrix<sup>19</sup> and has obtained oligomers with LC properties. In contrast to results from oligomers with oxyhexyl groups in side chains, oligomer I has only one transition temperature. The glass transition temperatures with increas-



**Figure 8** DSC curves of oligomers I, IV, and VI. Curve 1 pertains to oligomer I, curve 2 to oligomer IV, and curve 3 to oligomer VI.

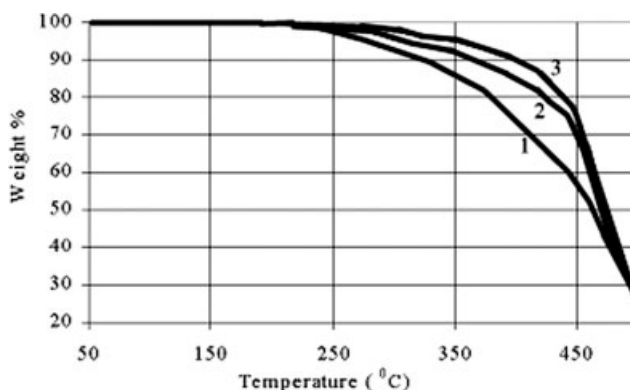
ing length of substituted alkyl groups are increasing from  $-112$  to  $+44^\circ\text{C}$ .

We have performed TGA runs in the air atmosphere. Return now to Table I. We conclude that the thermo-oxidative stability of oligomers is increased from  $270$ – $300^\circ\text{C}$  (oligomer I) to  $370$ – $390^\circ\text{C}$  (oligomer VI) with increasing the length of alkyl groups from hexyl to octadecyl in the side chain. In Figure 9 we present thermogravimetric curves for oligomers I, IV, and VI.

TGA provides several kinds of information.<sup>10</sup> One of them is the temperature at which 5% weight loss occurs. We conclude that the thermostability of our oligomers increases with the increase of the length of side chain alkyl groups. For polymethylsiloxane oligomers with hexyl and heptyl groups in the side chains this takes place at  $\sim 400^\circ\text{C}$ . The main destruction process proceeds in the temperature range  $500$ – $700^\circ\text{C}$ . After  $750^\circ\text{C}$  mass losses were not observed.

#### APPLICATIONS

We have demonstrated that a commercial polymethylhydrosiloxane can be used for our purposes together with a very inexpensive catalyst.



**Figure 9** Thermogravimetric curves of oligomers I (1), IV (2), and VI (3) (in air atmosphere).

We have prepared stationary phases for gas–liquid chromatography by using our synthesized oligomers. We have dried silica gel at 200°C under reduced pressure for 20 h before use. Silica was added to a THF solution of oligomers. For the preparation of stationary phases with the same concentration of repetitive unit per gram of silica, we obtained homogeneous suspension by vigorously stirring silica. Then we removed the solvent under vacuum at room temperature. The coated silica was finally dried under 0.01 Torr also at room temperature. The separation efficiency for hydrocarbons using so prepared stationary phases is under investigation.

As argued elsewhere,<sup>20</sup> gradual replacement of metallic parts by polymeric ones requires improved tribological properties of the latter. Work along these lines is ongoing, for instance, by Ehrenstein and co-workers<sup>21,22</sup> as well as in LAPOM.<sup>23–26</sup> There exists a variety of approaches to polymer reinforcement including introduction of ceramic fibers,<sup>27</sup> introduction of carbon nanotubes,<sup>28</sup> irradiation,<sup>22,29,30</sup> or imposition of magnetic fields.<sup>24</sup> Blending is one more such option<sup>31</sup> and we are planning, using oligomer VI as an additive to several engineering polymers, to see whether tribological properties can thus be improved.

## CONCLUSIONS

Hydrosilylation of  $\alpha,\omega$ -bis(trimethylsiloxy)methylhydrosiloxane to alkenes in the presence of a catalyst was performed at various temperatures and comb-type methylsiloxane oligomers with various alkyl substituted groups in the side chains have been obtained. It was shown that the reaction proceeds mainly according to the anti-Markovnikov and not all active  $\equiv\text{Si}-\text{H}$  groups participate in the hydrosilylation reaction.

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