

Formation of New Thermoreactive Polysiloxanes

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ABSTRACT: Hydrosilylation of α,ω -bis(trimethylsiloxy)-methylhydridesiloxane to propargyl alcohol in the presence of catalyst, platinum hydrochloric acid, was performed at several temperatures. Comb-type methylsiloxane oligomers with substituted reactive groups in the side chain have been obtained. At the high stages of reaction, gelation takes place. Except hydrosilylation, also proceeds dehydrocondensation reaction with low yield. The synthesized oligomers were characterized by $^1\text{H-NMR}$ spectroscopy. Calculations by quantum-mechanical semiempirical AM1 method for modeling reaction between methyl dimethoxysilane $[\text{Me}(\text{MeO})_2\text{SiH}]$ and propargyl alcohol were performed for fully characterization of hydride addition of

polymethylhydrosiloxane to propargyl alcohol. 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. Comb-type oligomers were characterized by gel-permeation chromatography, differential scanning calorimetry, thermogravimetry, and wide-angle X-ray diffraction analyses. Crosslinking of synthesized oligomer using γ -aminopropyltriethoxysilane was investigated and studied using DSC and TGA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2168–2173, 2007

Key words: polysiloxanes; functionalization of polymer; glass transition; hydrosilylation; crosslinking

INTRODUCTION

Polysiloxanes are characterized by a number of interesting properties, e.g., excellent heat resistance, low toxicity, biocompatibility, high oxygen permeability, poor wettability, extremely low surface tension, low melting point and glass transition temperature, resistance to radiation, special rheological properties, outstanding electrical isolating properties, and others.^{1,2} Polydimethylsiloxanes in which some methyl groups are replaced by reactive organofunctional groups are widely used. They have attracted much research and found useful applications, because it is a simple way to add new properties to the exceptional properties of silicones. Functional groups may be used to obtain new organic-silicone architectures. If the functional groups are distributed along the main chain, graft copolymers are obtained.³ Macromolecular grafting is a synthetic approach that involves the functionalization of a preformed polymer backbone containing reactive groups with an appropriate reagent. There is an increasing interest in catalytic grafting of polyhydrosiloxane as to an alternative route for the synthesis of organic-inorganic hybrid polymers, owing to the complexities involved in direct generation of well-defined linear hybrid polymers.⁴

Besides the process of equilibration, the hydrosilylation process is the most widely used method of preparing organofunctional polymethylsiloxanes starting from poly(methylhydro)siloxanes.^{5,6} Hydrosilylation of alkynes results in versatile materials for natural products⁷ and polymers.⁸ Selectivity is also an important consideration in the hydrosilylation of alkynes, because in addition to regioisomers and stereoisomers as legitimate products there is also the probability of obtaining diadducts.⁹ Hydrosilylation of alkynes offers a greater synthetic challenge of the triple bond and the potential for a broader product distribution.¹⁰ The majority of functionalized polysiloxanes were designed to undergo thermally induced crosslinking, and cure by hydrolytic processes or photochemically induced polymerization.¹

The properties of organosilicon polymers depend on the structure of macromolecular chains and on the nature of organic groups surrounding the silicon atom.¹¹

EXPERIMENTAL

Materials and techniques

The starting materials for the synthesis of thermoreactive comb-type methylorganosiloxane oligomers with functional groups in the side chain were α,ω -(bis-(trimethylsiloxy)methylhydrosiloxane and propargyl alcohol.

The initial α,ω -(bis(trimethylsiloxy)methylhydride)siloxane had the degree of polymerization $n \approx 35$,

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propargyl alcohol and catalyst H_2PtCl_6 were obtained from Aldrich and used as received. The organic solvents were cleaned by drying and distillation.

FTIR spectra were obtained on Nicolet Nexus 470 with MCTB detector. ^1H spectra were recorded on 400 MHz Bruker NMR spectrometer, using CDCl_3 as solvent and internal standard. Thermal gravimetric analysis was performed on a PerkinElmer TGA-7, the thermogravimetric analyzer, at $\sim 10^\circ\text{C}/\text{min}$. Differential scanning calorimetric analysis was performed on a PerkinElmer DSC-7. Heating and cooling scanning rates were $\sim 5^\circ\text{C}/\text{min}$.

Gel-permeation chromatography (GPC) investigations were performed using of Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastaygel columns. Sample concentration was $\sim 3\%$ by weight in toluene; a typical injection volume for the siloxane was $5\ \mu\text{L}$. Standardization of the GPC was accomplished by the use of styrene or polydimethylsiloxane standards with the known molecular masses.

Wide-angle X-ray diffractograms were taken on a DRON-2 (Burevestnik, Saint-Petersburg, Russia) instrument using A-CuK_α radiation. The values were measured without a filter, and the angular velocity of the motor was $\sim 2^\circ/\text{min}$.

Hydrosilylation of α,ω (bis(trimethylsiloxy)methylhydrosiloxane to propargyl alcohol

Hydrosilylation reaction was carried out in a two-necked flask, equipped with a magnetic stirrer, tube for catalyst inlet, and reflux condenser, which was connected to the equipment for measuring volume of eliminated hydrogen.

To the flask were added the following reaction products: 0.8677 g (0.00038 mmole) α,ω (bis(trimethylsiloxy)methylhydrosiloxane); 0.7519 g (0.0134 mmole) propargyl alcohol; and 4.2 mL dry toluene. The flask was placed inside an oil bath until constant temperature was reached. Then, the catalyst 0.1M solution of platinum hydrochloric acid in tetrahydrofuran ($5\text{--}9 \times 10^{-5}$ g/1.0 g of starting substance) was introduced. During the reaction, volume of eliminated hydrogen was measured. After the reaction, the solvent was eliminated via vacuum pump. During the high stages of reaction, gelation takes place; after evaporation of the solvent, 3 mL toluene has been added, and the soluble part was extracted; the yield of soluble polymer is 60% (0.88 g).

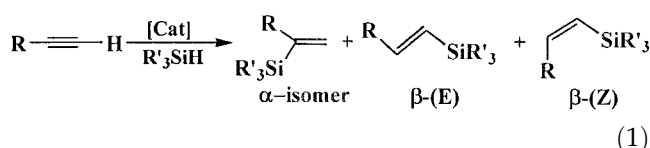
Cross-Linking using γ -aminopropyltriethoxysilane

The soluble part of the hydrosilylation product was dissolved in toluene at room temperature, and γ -

aminopropyltriethoxysilane was added (5% of oligosiloxane by weight). The solution, after 10-min stirring, was poured into a pan and placed in an oven for curing at 120°C for 12 h.

PROGRESS OF THE REACTION

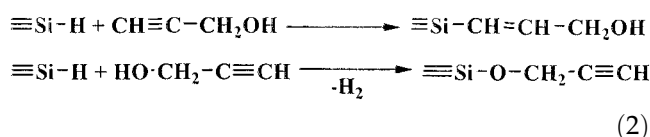
There is an extensive literature on hydrosilylation reactions of monomeric organohydrosilanes to propargyl alcohol. Products may contain three isomeric organosilanes obtained according to anti-Markovnikov rule (β -(E)- and β -(Z)-isomers) and Markovnikov rule (α -isomer). In general, we can represent this by the following scheme:^{12,13}



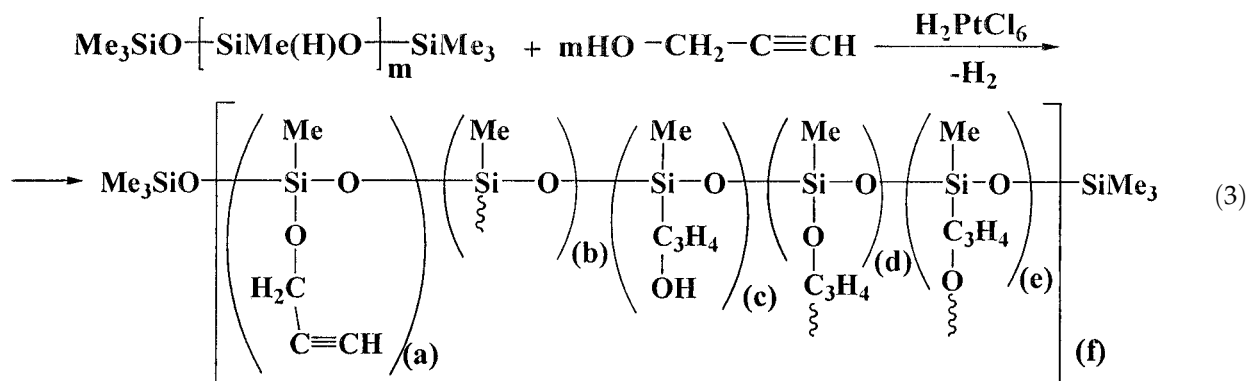
For the synthesis of comb-type oligomers, thermoreactive silicon-organic oligomers with functional groups in the side chain via hydrosilylation reaction of α,ω -bis(trimethylsiloxy)methylhydrosiloxane to propargyl alcohol and 0.1M solution of H_2PtCl_6 in THF were used. 1 : 35 was the ratio of the initial compounds.

Preliminary heating of initial compounds in the temperature range of $50\text{--}60^\circ\text{C}$ in the presence of catalyst showed that in these conditions there is no polymerization of propargyl alcohol, nor scission of siloxane backbones, nor elimination of methane from methylhydrosiloxane. No changes in the gel-permeation chromatograms, also in NMR and FTIR spectra of initial compounds, were found.

From the literature, it is known that platinum hydrochloric acid represents catalyst of as hydrosilylation reactions, as well as of dehydrocondensation reactions.¹⁴ Because of this, we have investigated hydrosilylation reactions in detail. As we mentioned earlier, in the literature are known the hydrosilylation reactions of propargyl alcohol with hydrosilanes. According to the literature data, during hydrosilylation, dehydrocondensation reactions do not take place.¹² In spite of this, we established that the next concurrent reactions proceed:



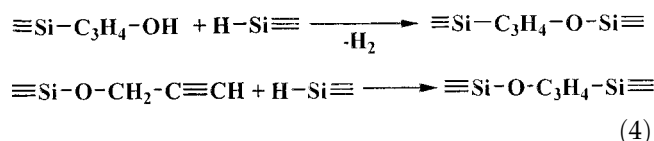
In general, we can represent hydrosilylation of α,ω -bis(trimethylsiloxy)methylhydrosiloxane with propargyl alcohol by the following scheme:



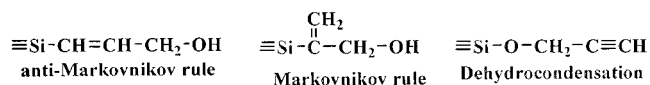
where, [(a) + (b) + (c) + (d) + (e)] (f) = $m \approx 35$; $I^1 = 50^\circ\text{C}$, $I = 60^\circ\text{C}$.

The synthesized oligomers are orange liquids. They are well soluble in ordinary aromatic type organic solvents with the specific viscosity $\eta_{\text{sp}} \approx 0.06\text{--}0.08$. The specific viscosity of initial polymethylhydrosiloxane is 0.05. Thus, it is evident that after modification specific viscosity rises. Structure and composition of the oligomers were established by elementary analysis, determination of molecular masses, by $^1\text{H-NMR}$ spectral data. Some physical-chemical properties of the synthesized oligomers are presented in Table I. We observe that after definite time at room temperature synthesized oligomers autocatalytically are crosslinked.

The reaction was carried out in the presence of toluene, but without solvent. Without solvent, the reaction proceeds vigorously by gelation, because of this, further reactions were carried out in toluene solution. During hydrosilylation reaction, branching process takes place with participation of residual (Si-H) groups in intermolecular crosslinking reactions by the following general scheme:

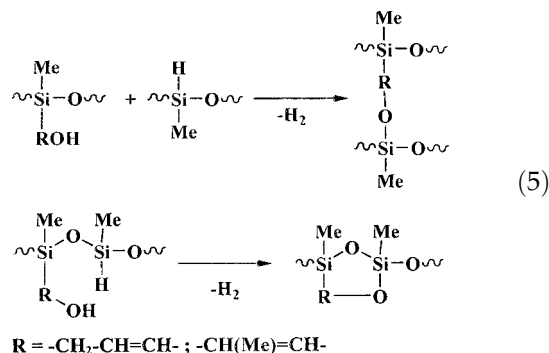


From the crosslinked system, the soluble part was extracted and investigated by NMR spectral analysis. In Table II, we present NMR spectra data for oligomer I.



From $^1\text{H-NMR}$ data, we infer that the hydrosilylation proceeds according to the anti-Markovnikov and Markovnikov rule. The ratio of the fragments obtained from the anti-Markovnikov and Markovnikov

rule is equal to 1 : 1. Also, spectral data show proceeding of dehydrocondensation, which is in agreement with experimental investigation. Signal for hydroxyl group with low intensity in the range $\delta \approx 4.7$ ppm is caused by the participation of the hydroxyl group in the branching process, according to the intermolecular and intramolecular dehydrocondensation reactions according to the following scheme:



We have carried out and investigated crosslinking of synthesized oligomer using γ -aminopropyltriethoxysilane, according to the technique described in Experimental section.

QUANTUM-MECHANICAL CALCULATIONS

Semiempirical quantum-mechanical methods are simplified versions of the Hartree-Fock approach using empirical (= derived from experimental data) corrections to improve performance. 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

TABLE I
Some Physical–Chemical Properties of Synthesized Oligomers

Symbol	Reaction temperature (°C)	Yield (%)	η_{sp}^a	M_w (10^{-3}); M_n (10^{-3}); (<i>D</i>)	T_g (°C)	Temperatures (°C) for 5% mass losses	d_1 (Å)	Elementary ^a composition (calcd/found) (%)		
								C	H	Si
<i>I</i> ¹	50	65	0.06	29.45; 6.4; (4.6)	+76	270	7.8	38.47/38.11	6.90/6.72	27.91/27.79
<i>I</i>	60	60	0.08	30.55; 6.5; (4.7)	+77	270	7.8	39.86/39.69	6.88/6.79	27.01/25.55

^a In 1% toluene solution at 25°C.

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 approximate quantum-mechanical model. For AM1, the parameterization is performed so that we obtain enthalpies of formation H^{form} , instead of total enthalpies¹⁵ as a function of the distance R_{C-Si} . The calculations provide us also with P_{x-y} values, which represent bond orders.

We have performed calculations by quantum-mechanical half empiric AM1 method for modeling reaction between methyldimethoxysilane [Me(MeO)₂SiH] and propargyl alcohol for fully characterization of hydride addition of polymethylhydrosiloxane to propargyl alcohol, using software Chem3D Ultra 9.0 from Cambridge Soft.

We consider the hydrosilylation of [Me(MeO)₂SiH] with propargyl alcohol in view of hydrosilylation according to the anti-Markovnikov rule and Markovnikov rule; we also consider dehydrocondensation reaction. We calculate activation energies (U_{act}) and formation enthalpies (H^{form}). Calculation method is described in our previous article.¹⁶ In Table III are presented the activation energies and the formation enthalpies for reaction according to hydrosilylation (anti-Markovnikov rule and Markovnikov rule) and dehydrocondensation.

Now compare formation enthalpies. Clearly, reaction of methyldimethoxysilane to propargyl alcohol is more favorable according to hydrosilylation. Also, the possibility of proceeding hydrosilylation according to the anti-Markovnikov and Markovnikov rule is equal. This result is in agreement with experimental data.

TABLE II
¹H-NMR δ (ppm) of Oligomer I

Si–CH ₃	0.1
Si(CH ₃) ₃	0.2
–C≡CH	2.5
–CH ₂ –O–Si≡	3.9
–CH ₂ –OH	4.1
–CH ₂ –OH	4.7
=C=CH ₂	5.5
≡Si–CH=	5.8
Si–CH=CH–	6.3

GEL-PERMEATION CHROMATOGRAPHY RESULTS

The synthesized oligomers were studied by GPC. Figure 1 shows the molecular weight distribution of oligomer I. A trimodal curve is seen. We find the number average molecular mass $M_n \approx 6.5 \times 10^3$ and the weight average molecular mass $M_w \approx 30.55 \times 10^3$. Thus, the polydispersity index is equal to 4.7. Compare now the weight average molecular masses of initial polymethylhydrosiloxane and oligomer I. The weight average molecular mass of initial polymethylhydrosiloxane is equal to $M_w \approx 2.39 \times 10^3$ and the polydispersity is equal to 1.18. From the polydispersity index of products, it is evident that polydispersity rises ~ 4 times, which is caused by branching processes.

The average molecular weight of synthesized oligomer I exceed ~ 8 times the theoretical value calculated for the full hydrosilylation. This indicates that branching processes take place during the reaction. Branching process is caused by intermolecular reactions, which we discussed earlier (Scheme 4). Also, the difference in appearance and degree of crosslinking can be attributed to the effectiveness of the different Pt–species of H₂PtCl₆, which cannot be separated from oligomers after reaction. Pt is partially in the form of Pt(II). It reacts with the (Si–H group of the PMHS backbone with the elimination of hydrogen and producing Pt metal. This fact leads us to suggest that crosslinking also occurs according to the following scheme:^{16–18}

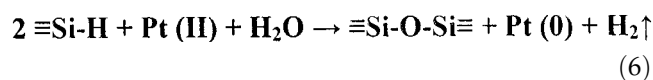


TABLE III
Formation Enthalpies and Activation Energies Modeling Hydrosilylation–Dehydrocondensation Reaction with Methyldimethoxysilane to Propargyl Alcohol

Reaction direction	Formation enthalpies H^{form} (kJ/mol)	Activation energy U_{act} (kJ/mol)
Markovnikov rule	–191.0	185.5
Farmer rule	–190.2	185.0
Dehydrocondensation	–76.0	224.0

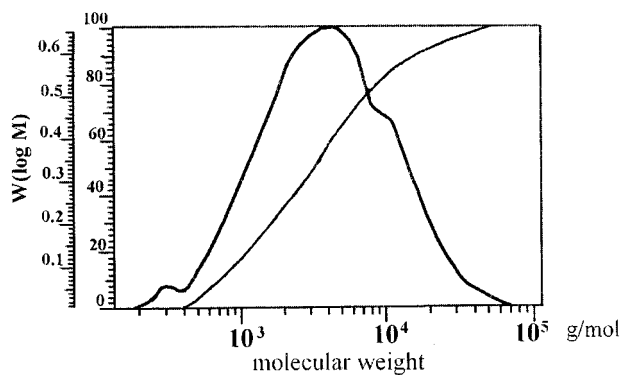


Figure 1 Gel-permeation chromatographic curves for oligomer I.

In the FTIR spectrum, we find signal with low intensity in the region 1187 cm^{-1} , which is characteristic for silsesquioxane bonds ($\text{SiO}_{3/2}$) and shows about side reactions due to crosslinking. Crosslinking in this way proceeds with low degree.

CALORIMETRIC RESULTS: DSC AND TGA

We show in Figure 2 the DSC results for oligomer I (curve 1) and for crosslinked system (curve 2). In the case of oligomer I, there is only one endothermic peak, which corresponds to the glass transition temperature $T_g \approx 77^\circ\text{C}$. High glass transition temperature (glass transition temperature of initial polymethylhydrosiloxane is equal to -113°C) shows about crosslinking in polymer by the formation rigid system. After crosslinking, using γ -aminopropyltriethoxysilane, glass transition temperature of the polymeric system increases up to 159°C .

We have performed TGA in air and also in nitrogen atmosphere. We present that 5% mass losses in air atmosphere are observed at $\sim 270^\circ\text{C}$ (Table I). The main thermo-oxidative destruction process proceeds in the range $300\text{--}480^\circ\text{C}$. In Figure 3, we show thermogravimetric curves for oligomer I and cross-linked system in nitrogen atmosphere.

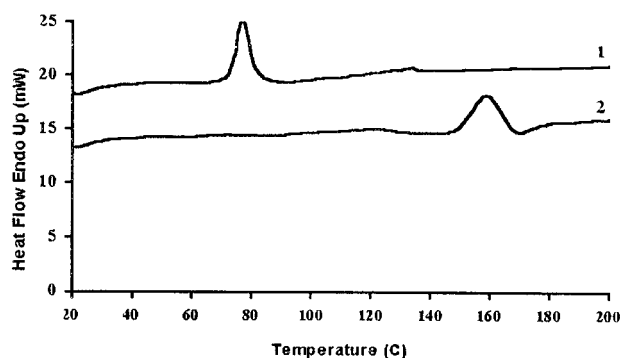


Figure 2 DSC curve of oligomer I (1) and for crosslinked system.

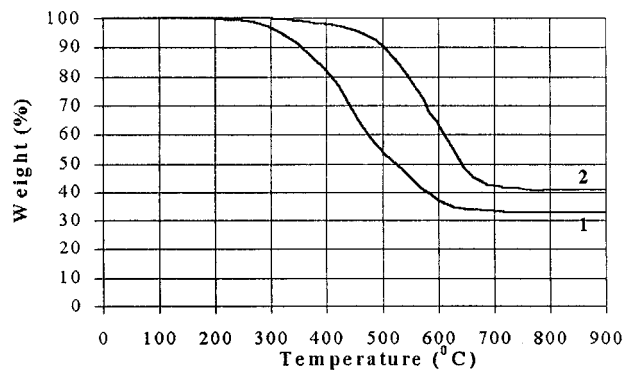


Figure 3 Thermogravimetric curves of oligomer I (1) and crosslinked polymer (2)

TGA provides several kinds of information.¹⁹ One of them is the temperature at which 5% weight loss occurs. For synthesized oligomer I in nitrogen atmosphere, this takes place at $\sim 320^\circ\text{C}$. Crosslinking using γ -aminopropyltriethoxysilane increases thermal stability of polymer ($\sim 480^\circ\text{C}$).

POSSIBLE APPLICATION

Functionalized siloxane monomers and 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, adhesives, and as release agents.²⁰ We are testing obtained oligomers as thermal crosslinking agents for several thermoplastic polymers and for several composites. Synthesized oligomers can be used as matrices for obtaining of new polysiloxanes on the basis of functional groups in the side chain.

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