Synthesis of New Methylsiloxane Oligomers with Pendant Trialkoxysilylethyl Groups for Preparation of Silicon hard Coatings

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Summary: For the purpose to prepare precursor materials for the silicon hard coatings, the hydrosilylation reactions of α, ω–bis(trimethylsiloxy)methylhydride-siloxane to trialkoxyvinylsilanes in the presence of platinum hydrochloric acid (0.1 M solution in THF), Karstedt's catalyst ($Pt_2[(VinSiMe_2)_2O]_3$) and platinum on the carbon (5%) were investigated. Hydrosilylation reactions at different ratios of initial compounds and at various temperatures (40–60 °C) were investigated and methylsiloxane oligomers with pendant trialkoxy fragments have been obtained. It was shown that completely hydrosilylation of all active ≡Si–H groups do not take place. The hydrosilylation reaction order, activation energy and rate constants were determined. The synthesized oligomers were characterized by ^1H, ^{13}C NMR and FTIR spectra data. Gel-permeation chromatography, differential scanning calorimetric, thermogravimetric and wide-angle X-ray investigations of synthesized oligomers were carried out. Synthesized oligomers together with tetraethoxysilane were used for preparation of silicon hard coatings via sol-gel processes.

Keywords: coatings; cross-linking; hydrosilylation; kinetics; methylhydrosiloxane oligomers

Introduction

Polymers are distinguished by their low density, flexibility, ease of manufacture, and cost-effectiveness. However, their surface properties often do not meet the demands regarding scratch-resistance, wettability, biocompatibility, gas transmission, adhesion, or friction. Hence, an additional surface modification and covering is required to achieve the desired properties, while maintaining the characteristics of the volume.[1–3]

Silicon polymers have received much attention as high performance and functional polymers. Polysiloxanes with excellent low temperature flexibility and high temperature stability derived from ≡Si–O–Si≡ skeleton have been widely used as elastomers and plastics in various industries. Polysiloxanes are also widely used in coatings to improve mechanical and chemical resistance of the surface (scratch- and abrasion-resistance), also they are used as interfacial modifiers to improve properties such as wetting and adhesion.[4–6] In recent years, alkoxysilane are widely used in organic/inorganic coatings known as ceramers.[7–10] Alkoxysilane can hydrolyze via reacting with water and condense to form ≡Si–O–Si≡ bonds due to three dimensional structures (SiO_2).

EXPERIMENTAL

2.1. Materials

Polymethylhydrosiloxane, platinum hydrochloric acid, Karstedt's catalyst ($Pt_2[(VinSiMe_2)_2O]_3$) (platinum(0)-1,3-divinyl-1,1,3, 3-tetramethyldisiloxane complex solution in PDMS), platinum on the carbon,

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trimethoxyvinylsilane, triethoxyvinylsilane and tetraethoxysilane were purchased from Aldrich and were used as received. Toluene was dried over and distilled from sodium under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. 0.1 M solution of platinum hydrochloric acid in THF was prepared and kept under nitrogen at low temperature.

Hydrosilylation Reaction of PMHS with Trimethoxyvinylsilane in the Presence of H_2PtCl_6

Polymethylhydrosiloxane (0.7681 g, 0.3395 mmol), trimethoxyvinylsilane (2.2681 g, 11.93 mmol) and 5.0 ml dry toluene were placed into the three-necked flask equipped with a magnetic stirrer, reflux condenser and thermocouple. Then the catalyst 0.1 M solution of platinum hydrochloric acid in tetrahydrofuran ($5 - 9 \cdot 10^{-5}$ g per 1.0 g of starting substance) was introduced. After the reaction completed, the solvent was partially eliminated, the reaction product was precipitated from toluene solution by n-hexane, and 2.8 g (92%) oligomer was obtained. The hydrosilylation reactions in the presence of other catalysts were carried out according to the above-mentioned method.

2.3. Preparation of Silicon Hard Coatings

Hydrolysis of tetraethoxysilane was carried out in alcohol solution in the presence 0.02 N HCl solution (ratio - $Si(OC_2H_5)_4$: C_2H_5OH: 0.02N HCl = 2,2:1:1). After 18 hours to the prepared solution was added acetic acid (concentration 15%) with amount 0,8% from total weight and oligomer I^1 with amount of initial total weight. After 4 hour, under stirring 2-propanol and water were added and siloxane hydrogels were obtained. Silicon hard coatings were prepared according to the following:

1. PC sheets were washed by ALCONOX and distilled water, after they were washed by 2-propanol and dried with nitrogen. After mixing completion the washed sheets were spin-coated (v = 1.0) with prepared mixtures and immediately placed in oven at temperature 100 °C during 5 hours (Coating 1).
2. PC sheets before decomposition of prepared silicon hard coats were cleaned. First they were washed by ALCONOX soup and water, after with iso-propanol and dried with nitrogen. After PC sheets were primed with CT-510 to improve adhesion (methacrylate coating). After mixing completion the sheet was spin-coated (v = 1.0) with prepared mixtures and immediately placed in oven at temperature 100 °C during 5 hours (Coating 2).

2.4. Determination of ≡Si–H Content

We calculate the content of active ≡Si–H groups in oligomers on the basis of the following reaction:

$$2\equiv\mathrm{Si}-\mathrm{H}\xrightarrow{\substack{\text{KOH alcohol}\\ \text{solution}}}\equiv\mathrm{Si}-\mathrm{O}-\mathrm{Si}\equiv+\mathrm{H}_2\uparrow$$

We place in a two-necked flask an exactly weighed amount of ≡Si–H containing oligomer, which should correspond to evolution of certain volume of hydrogen gas. We fit pressure-equalized dropping funnel with 0.5 M KOH alcohol solution onto the flask. We connect the flask with a gas buret, which we connect with a levelling bottle at the bottom part, by means of a silicon tube. We allow the system to stand for 10 min. The water level in the levelling bottle adjusts to the same level as that in the gas buret (V_1, ml) is recorded. After, we add the 0.5 M KOH alcohol solution slowly. As hydrogen gas evolves, the water level; goes downward. Thus, we need to keep the both water levels the same as each other so that we could equalize the pressure in the system to atmosphere. After the evolution of hydrogen gas completes (around 3–5 min) we record another 5 min later the value of the water level in the buret (V_2, ml). The difference between V_2 and V_1 gives the volume of eliminated hydrogen gas (V, ml). The Si–H content of an oligomer is given by the following:

$\equiv$Si–H content% = 1000 PV/WRT (mol/100g)

Where p – atmospheric pressure at measurement (atm), V – gas volume captured (ml), W – sample weight (g), R = 0.0082 (gas constant) ($l \cdot atm \cdot mol^{-1} \cdot K^{-1}$), and T – temperature (K at measurement).[13]

Characterization

FTIR spectra were recorded on a Nicolet Nexus 470 machine with MCTB detector. ^{1}H, ^{1}H-^{1}H COZY, ^{13}C NMR and H,C-correlation NMR spectra were recorded on a 500 MHz Bruker NMR spectrometer, using $CDCl_3$ as the solvent and an internal standard. Differential scanning calorimetric investigation (DSC) was performed on a Perkin Elmer DSC-7 apparatus. Thermal transitions including glass transition temperatures T_g were taken as the maxima of the peaks. The heating and cooling scanning rates were 10 K/min.

Wide-angle X-ray diffractograms were taken on a DRON-2 (Burevestnik, Saint Petersburg, Russia) instrument. A-CuK_α was measured without a filter; the angular velocity of the motor was $\omega \approx 2$ deg/min.

Results and Discussion

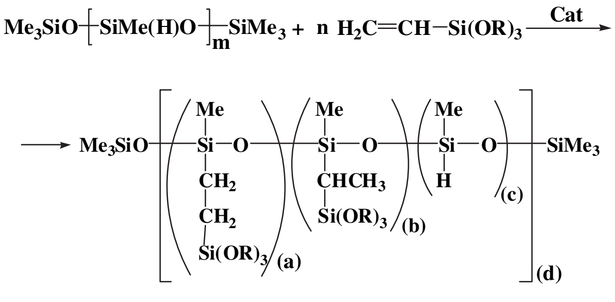
For the purpose to synthesize precursor materials for silicon hard coatings we synthesized comb-type siliconorganic oligomers with different trialkoxysilylethyl groups in the side chain by hydrosilylation reactions of polymethylhydrosiloxane with trialkoxyvinylsilanes. In such way we have obtained oligomers with prefabricated siloxane backbone and with pendant trialkoxysilylethyl groups, which can participate in hydrolysis-dehydrocondensation reactions due to formation 3D structure.

Hydrosilylation reactions of polymethylhydrosiloxane with trialkoxyvinylsilanes were carried out in the presence of different catalysts: Karstedt's catalyst ($Pt_2[(VinSiMe_2)_2O]_3$ in PDMS), platinum hydrochloric acid (0.1 M in THF) and platinum on the carbon. We have used polymethylhydrosiloxane with different length of siloxane backbone ($n \approx 35$ and 65). For the purpose to utilize all active $\equiv$Si–H bonds reactions were carried out with various molar ratios of initial compounds (1:1, 1:1,5 and 1:2 in view of $\equiv$Si–H bonds).

Preliminary heating of initial compounds in the temperature range of 50 – 85 °C in the presence of catalysts showed that in these conditions there is no polymerization of trialkoxyvinylsilanes, nor destruction of siloxane backbone, nor dehydrocondensation reactions via alkoxy groups. No changes in the NMR, FTIR and GPC spectra of initial compounds were found.

We have carried out above mentioned reactions in the melt, but reactions proceed vigorously (especially in case of platinum hydrochloric acid and Karstedt's catalyst) and in low stages of $\equiv$Si–H bonds' conversion (~30 – 40%) gelation takes place via intermolecular hydrosilylation dehydrocondensation. For prevention of gelation and for investigation of kinetic parameters we have carried out reactions in the absolute dry toluene.

In general, hydrosilylation of α(ω–bis (trimethylsiloxy)methylhydrosiloxane to trialkoxyvinylsilanes proceeds according



to the following scheme:
Where: m ≈ 35 and 65, [(a)+(b)+(c)]x (d) = m; R=CH_3 [I^1 - m ≈ 65, 85 °C (H_2PtCl_6); I^2 - m ≈ 65, 85 °C (Karstedt's catalyst)]; C_2H_5 [II^1 - m ≈ 35, 50 °C; II^2 - m ≈ 35, 60 °C; II^3 - m ≈ 35, 70 °C; catalyst - H_2PtCl_6; molar ratio of initial compounds 1:35. II^4 - m ≈ 35, 70 °C; I catalyst – platinum on the carbon; molar ratio of initial compounds 1:35. II^5 and II^6 - 50 °C, catalyst - H_2PtCl_6; molar ratio of initial compounds accordingly 1:70 and 1:105]; C_2H_5 [III^1 - m ≈ 65, 85 °C (H_2PtCl_6); III^2 - m ≈ 65, 85 °C ((Karstedt's catalyst)].

The synthesized oligomers are vitreous liquid products, which are well soluble as in aromatic solvents, also in alcohols. Structures and compositions of the oligomers were established by elementary and functional analyses, FTIR spectra, ^1H, ^{13}C, H,H-COSY and C,H-correlation NMR spectra data. Synthesized polysiloxanes were characterized by differential scanning calorimetric, thermogravimetric and wide-angle X-ray diffractometric methods. Some characteristic data for hydrosilylation reaction and synthesized oligomers are presented in Table 1.

During the hydrosilylation reaction, decrease of active ≡Si–H groups' concentration with time was observed. The hydrosilylation reactions were performed in dry toluene solution (C ≈ 5.0 · 10-2 mol/l). In Fig. 1 we show changes of concentration of active ≡Si–H groups with time in case of hydrosilylation reactions of polymethylhydrosiloxane (n ≈ 35) with vinyltriethoxysilane in the presence of H2PtCl6 with 1:35 molar ratios of initial compounds (1:1 stoichiometric relationships between initial compounds in view of ≡Si–H bonds). From Fig. 1 it is evident that at 50 °C hydrosilylation reaction proceeds with ~84% conversion of active ≡Si–H groups, whereas at 70 °C hydrosilylation reaction proceeds with ~90% conversion. Consequently, with the rise of temperature, the depth of hydrosilylation reaction increases.

Fig. 2 shows dependence of the reverse concentration of ≡Si–H groups on the time during the hydrosilylation reaction of α, ω–bis(trimethylsiloxy)methylhydrosiloxane with vinyltriethoxysilane. One can see that at the initial stages the hydrosilylation reaction is of second order. The reaction rate constants of hydride addition reactions of polymethylhydridesiloxane to vinyltriethoxysilane at various temperatures were determined (reaction rate constants are equal of tangents of the angels taking in view the value of x and y axis): k70 °C ≈ 0,1171, k60 °C ≈ 0,0598 and k50 °C ≈ 0,0301 mol · l-1 · s-1. The reaction temperature coefficient is equal to γ = 2.

We have calculated the activation energy for the reactions using logarithmic

Table 1.
Some physical chemical properties of synthesized oligomers.

Oligomer No	Catalysts	Reaction temperature/°C	Yield %	η_{sp}*	T_g °C	Temperatures/°C for 5% mass losses	Elementary analysis		
							C	H	Si
I^1	H_2PtCl_6	85	90	–	−64	350	$\frac{42.35}{42.15}$	$\frac{8.56}{8.75}$	$\frac{23.90}{23.77}$
I^2	Karstedt's	85	95	–	−65	350	$\frac{42.76}{43.38}$	$\frac{8.82}{8.76}$	$\frac{23.40}{23.56}$
II^1	H_2PtCl_6	50	92	0.07	–	–	$\frac{42.48}{42.54}$	$\frac{8.25}{8.78}$	$\frac{23.74}{23.35}$
II^2	H_2PtCl_6	60	91	0.07	–	–	–	–	–
II^3	H_2PtCl_6	70	91	0.08	–	–	$\frac{42.46}{●42.72}$	$\frac{●8.53}{●8.73}$	$\frac{●23.09}{●23.15}$
II^4	Pt/C	70	92	0.07	−63	–	●–	●–	●–
II^5	H_2PtCl_6	50	93	0.08	–	–	●–	●–	●–
II^6	H_2PtCl_6	50	94	0.08	–	–	$\frac{●41.46}{●40.98}$	$\frac{●8.70}{●8.64}$	$\frac{●24.88}{●25.03}$
III^1	H_2PtCl_6	85	91	–	–	370	●–	●–	●–
III^2	Karstedt's	85	95	–	−65	370	●–	●–	●–
IV	H_2PtCl_6	50	92	0.07	–	–	$\frac{●42.12}{●42.65}$	$\frac{●9.10}{●9.03}$	$\frac{●27.02}{●26.56}$

* In 1% toluene solution at 250C.

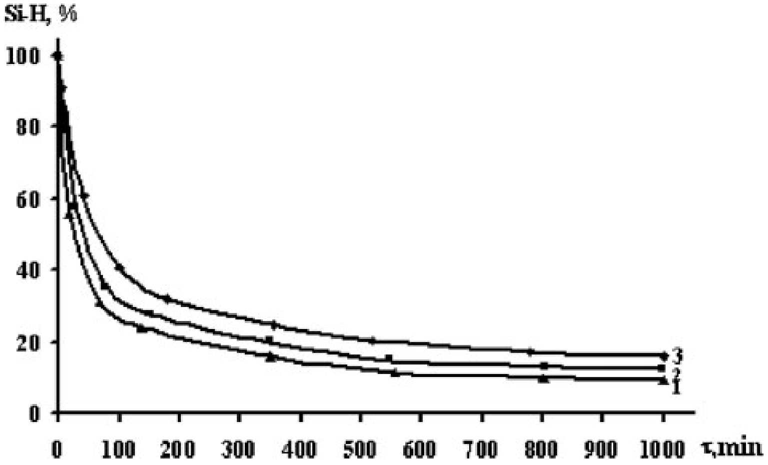


Figure 1.
Dependence of changes of concentration of active ≡Si–H groups on the time, during hydrosilylation reactions of polymethylhydrosiloxane with vinyltriethoxysilane, where curve 1 represents the values obtained at 70 °C, curve 2 represents the values obtained at 60 °C and curve 3 represents the values obtained at 50 °C (Catalyst - H_2PtCl_6).

reaction rate constants as functions of the reverse temperature (Fig. 3). The activation energy is equal to $E_{act} \approx 41{,}5$ kJ/mol.

Hydrosilylation reactions of polymethylhydrosiloxane to vinyltriethoxysilane were studied as with stoichiometric ratio (1:35), also with ratios 1:70 and 1:105 (accordingly 1:2 and 1:3 molar ratios of initial compounds in view of ≡Si–H bonds). In Fig. 4 are presented the changes of concentration of active ≡Si–H groups on the time, during hydrosilylation reactions of polymethylhydrosiloxane to vinyltriethoxysilane at the same temperature in case of different ratios (50 °C).

We can conclude from the above mentioned results that hydrosilylation of polymethylhydrosiloxane with vinyltriethoxysilane in case of stoichiometric relationship proceeds with less conversion of active ≡Si–H bonds, than in case of excess of vinyltriethoxysilane 2- and 3-times. But also

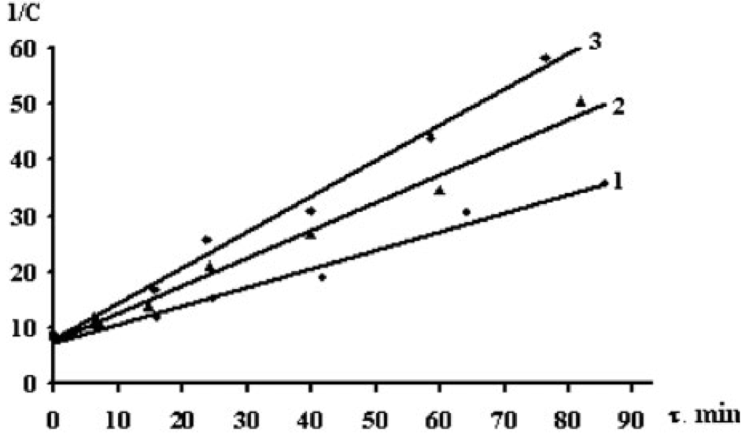


Figure 2.
Dependence of reverse concentration of ≡Si–H groups on time during the hydrosilylation reaction of polymethylhydrosiloxane to vinyltriethoxysilane.

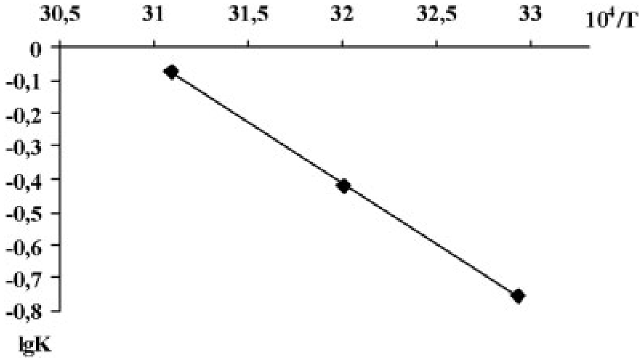


Figure 3.
Dependence of reaction rate constants' logarithm on the reverse temperature during hydrosilylation of polymethylhydridesiloxane to vinyltriethoxysilane.

it is evident that there is a little difference in results of ≡Si–H bonds' conversion between 2- and 3-times excess of vinyltriethoxysilane.

In the Fig. 5 is presented changes of concentration of active ≡Si–H groups during the hydrosilylation reactions of polymethylhydrosiloxane with vinyltriethoxysilane at the 70 °C temperature in the presence of platinum hydrochloric acid (0.1 M in THF) and platinum on the carbon, the ratio is 1:70. From the Fig. 5 it is evident that activity of the catalyst of platinum hydrochloric acid exceeds the activity of platinum on the carbon, because in the presence of platinum hydrochloric acid the conversion of active ≡Si–H groups is equal to ~93.6%, while in the presence of platinum on the carbon – 70.5%. In case of Karstedt's catalyst reaction undergoes with ~100% conversion of active ≡Si–H groups.

In the FTIR spectra of oligomer I[1] we observe absorption bands in the regions 765, 1200, 1265 and 1025 cm^{-1}, which are

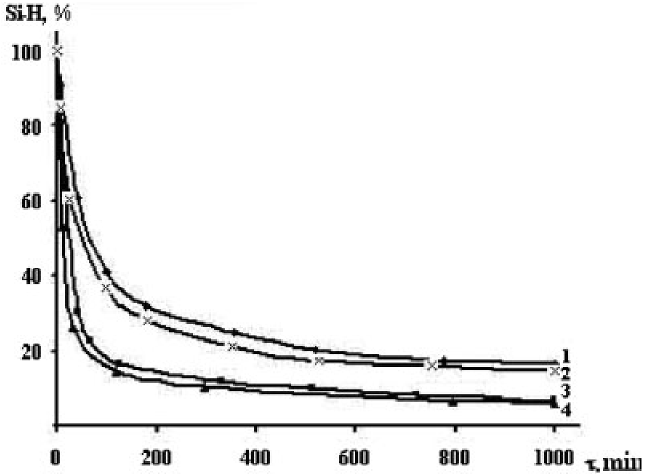


Figure 4.
Changes of concentration of active ≡Si–H groups during the hydrosilylation reactions of polymethylhydrosiloxane with vinyltriethoxysilane at the 50 °C temperature in case of different ratios (Catalyst - H_2PtCl_6). Curve 1 represents the values obtained at ratio 1:35, curve 3 represents the values obtained at 1:70 and curve 4 represents the values obtained at 1:105 ratio. Curve 2 corresponds to hydrosilylation of polymethylhydrosiloxane to methylvinyldiethoxysilane at the 50 °C temperature in case of 1:35 ratio.

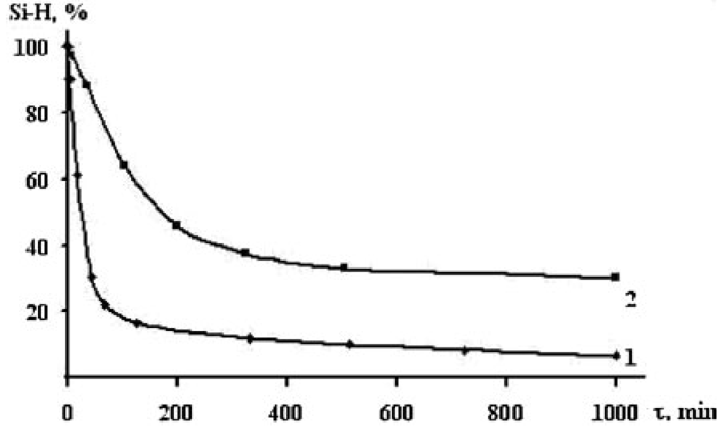


Figure 5.
Changes of concentration of active ≡Si–H groups during the hydrosilylation reactions of polymethylhydrosiloxane with vinyltriethoxysilane at the 70 °C temperature, with 1:70 ratio of initial compounds. Curve 1 represents the values obtained in the presence of H_2PtCl_6, curve 2 represents the values obtained in the presence of platinum on the carbon.

characteristic for -$SiMe_3$, ≡Si–CH_2–, ≡Si–Me and ≡Si–O–Si≡ bonds. In addition, we observe an absorption band in the region 2165 cm^{-1} characteristic for unreacted ≡Si–H bonds. Here we want to mention that this signal is not observed in case of oligomer I^2, which is obtained in the presence of Karstedt's catalyst with 1:70 ratio of initial compounds.

In the Fig. 6 is given ^1H and H,H-COSY NMR spectra of oligomer I^2, where one can observe singlet signals for protons in ≡Si–Me and –$SiMe_3$ groups with chemical shifts $\delta \approx 0.02$ ppm and $\delta \approx 0.03$. In the ^1H spectra of oligomer I^2 one can observe signals characteristic for methyl protons of the fragment =CH–CH_3 with chemical shift $\delta \approx 0.9$ ppm, signal $\delta \approx 1.12$ ppm characteristic for methylene protons of the fragment ≡Si–CH_2–, signal with chemical shift $\delta \approx 1.46$ ppm characteristic for methylene protons of the $(CH_3O)_3Si–CH_2$– fragment, signal with chemical shift $\delta \approx 1.86$ ppm characteristic for methine protons in the

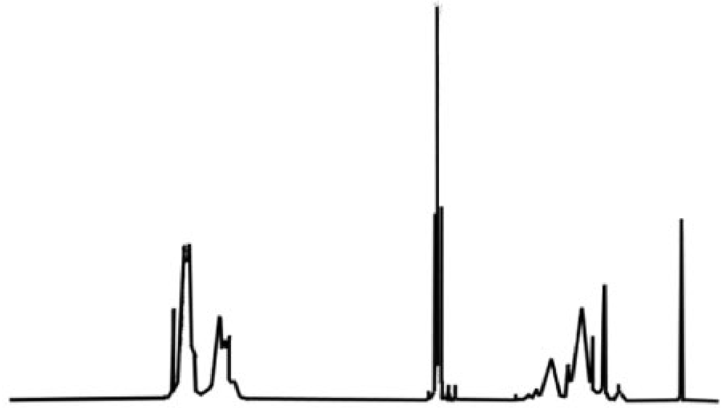


Figure 6.
^1H NMR spectra of oligomer I^2.

$=CH–CH_3$ fragment and signal $\delta \approx 3.5$ ppm for methyl protons of OCH_3 group. In addition we want to mention that in the spectra there is no signal characteristic for $\equiv$Si–H bonds in the range 4.1–4,5 ppm. ^{1}H NMR spectra shows that hydrosilylation reaction mainly proceeds according to anti-Markovnikov rule, as well as according to Markovnikov rule with low degree of conversion. In the ^{1}H NMR spectra of oligomer I^1 in addition we can observe singlet signal with chemical shift $\delta \approx 4.2$ ppm with low intensity, which proves that in the presence of platinum hydrochloric acid hydrosilylation of all active $\equiv$Si–H bonds do not take place.

In the Figure 7 and 8 are presented ^{1}H, H,H-COSY, ^{13}C and C,H-correlation NMR spectra of oligomer II^3. In the ^{1}H and H,H-COSY NMR spectra (Fig. 8) one can observe singlet signals for protons of $\equiv$Si–Me and $–SiMe_3$ fragments with chemical shifts $\delta = 0.2$ ppm and $\delta = 0.3$ ppm accordingly. In spectra one can observe triplet signal with chemical shift $\delta = 0.45$ for methylene protons of $\equiv Si–CH_2–$ fragment, signal $\delta = 0.95$ ppm for methyl protons of $–CH–CH_3$ fragment, signal with chemical shift $\delta = 1.15$ ppm for methylene protons in $(CH_3O)_3Si–CH_2–$ fragment and multiplet signal $\delta = 1.35$ ppm for methine protons of $=CH–CH_3$ fragment. In addition in spectra one can observe signal with chemical shift $\delta = 3.8$ characteristic for methylene protons in $–CH_2O–$ group. In spectra takes place overlapping of signals characteristic for

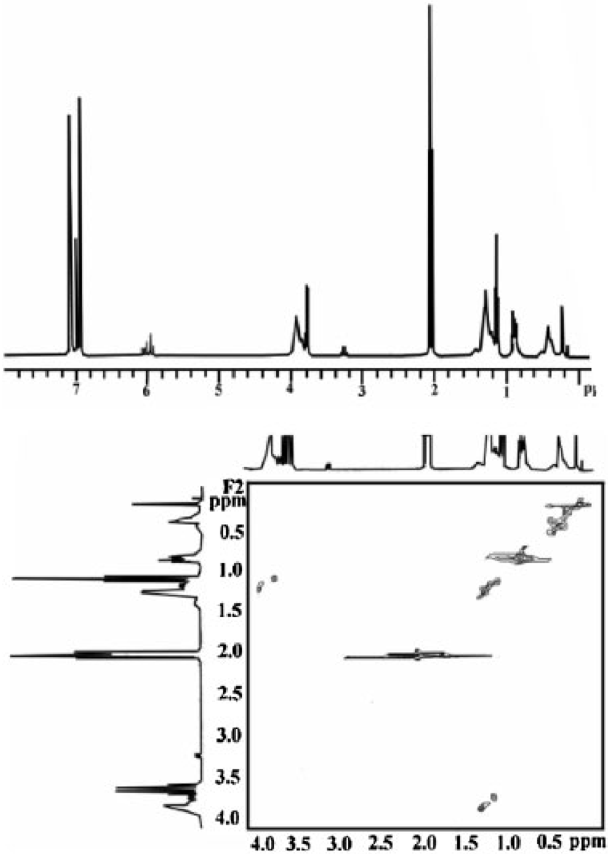


Figure 7.
^{1}H and H,H-COSY NMR spectra of oligomer II^3.

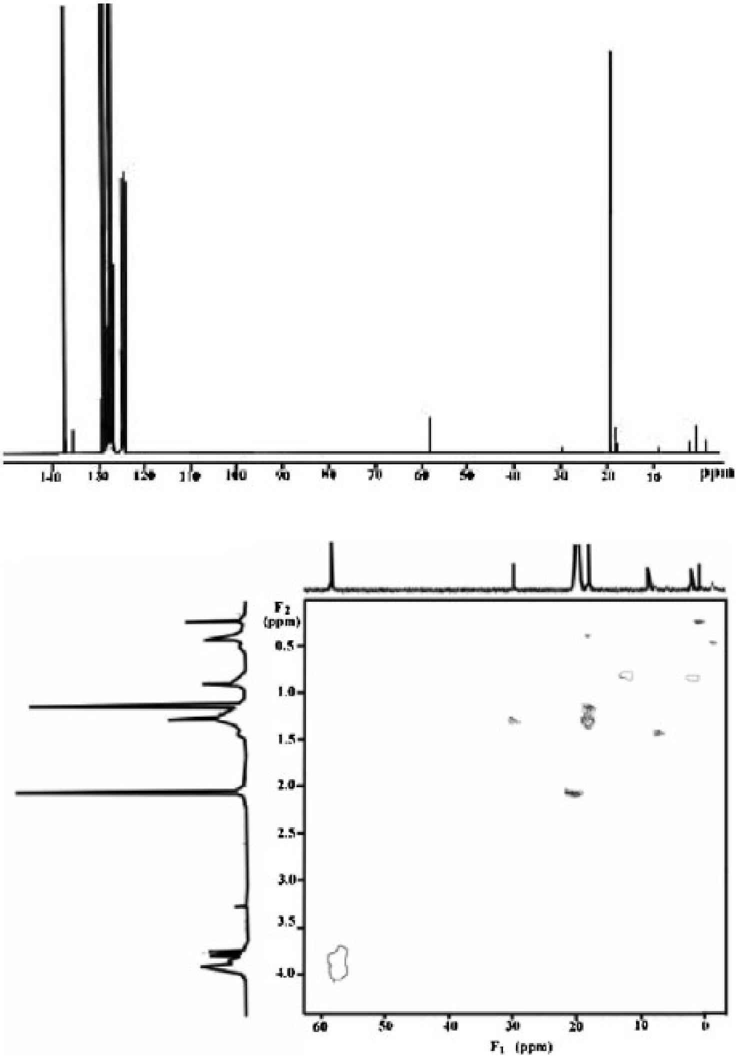


Figure 8.

^{13}C and C,H-correlation NMR spectra of oligomer II^3.

methyl protons of CH_3CH_2O– and $=CH–CH_3$ fragments. ^1H and H,H-COSY NMR spectra shows that reaction mainly proceeds according to anti-Markovnikov rule, but with low degree reaction also proceeds by Markovnikov rule.

In the ^{13}C and C,H-correlation NMR spectra of oligomer II^3 (Fig. 8) is in full agreement with ^1H and H,H-COSY NMR spectra data and proves proceeding of hydrosilylation according to both, anti-Markovnikov and Markovnikov rules. In spectra one can observe signal $\delta = 59.0$ for carbon in $–CH_2O–Si\equiv$ fragment, signal $\delta = 30.0$ ppm characteristic for methine carbon of $=CH–CH_3$ fragment, for carbon in $\equiv Si–CH_2–$ signal $\delta = 18.2$ ppm, signal $\delta = 18.0$ ppm for methylene carbon in fragment $(CH_3O)_3Si–CH_2–$ and signal $\delta = 9.0$ ppm for methyl carbon in $=CH–CH_3$ fragment.

Synthesized oligomers were characterized by DSC (Figure 9). There are only single endothermic peaks which correspond to the glass transition temperatures (see Table 1).

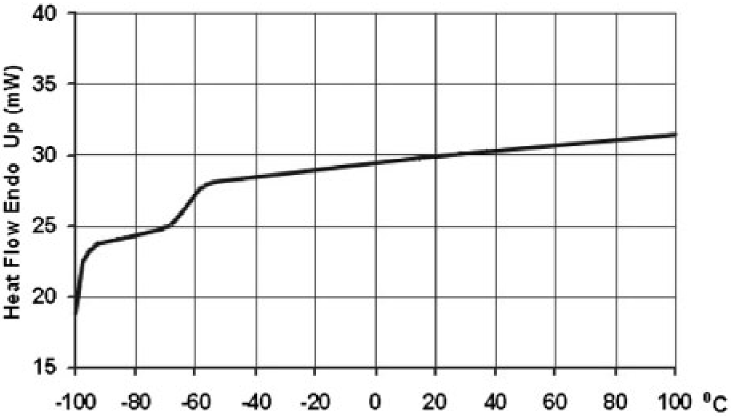


Figure 9.
DSC curve of oligomer I^2.

For synthesized oligomers the thermogravimetric investigations were carried out. On the Figure 10 thermogravimetric curves of oligomers I^1 and III^1 are presented, which indicate that these oligomers are characterized with high thermal stability and 5% mass losses are observed at 350 °C and 370 °C accordingly. The main destruction process of synthesized oligomers proceeds in the temperature range 370–550 °C.

Synthesized oligomer I^1 was used for preparation of silicon hard coating, which was prepared for covering of polycarbonate sheets. Preparation technology is in details described in section 2.3. For coated PC sheets we have carried out anti-abrasion analyses. In the Figure 11 is shown dependence of haze on the abrasion cycles.

From the Figure it is evident that using of acrylic primer Techneglas CT-510 improves mechanical properties of the surface of prepared silicon hard coating. Also we want to mention that prepared coating during first 100 cycles is more transparent than coating of company.

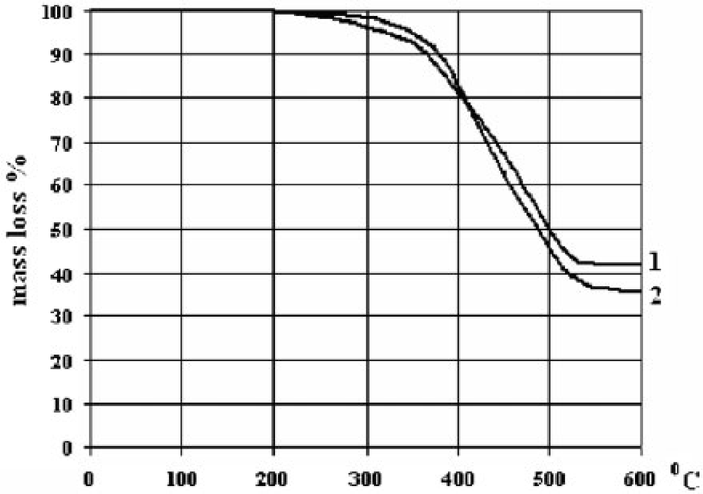


Figure 10.
Thermogravimetric curves of oligomers I^1 and III^1 (curve 1 corresponds to oligomer I^1 and curve 2 corresponds to oligomer III^1).

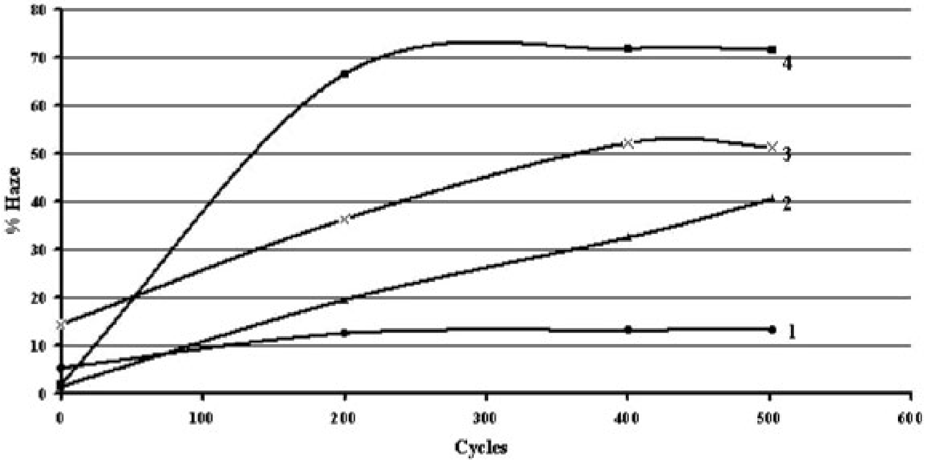
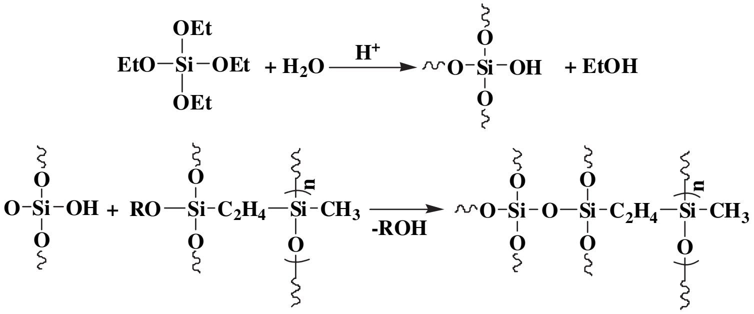


Figure 11.
dependence of haze % on the abrasion cycles. Curve 1 pertains to wide used coated polycarbonate sheet. Curve 2 – to the Coating 2, curve 3 – Coating 1, curve 4 – uncoated PC sheet.



The sol-gel process during preparation of coating includes two stages: hydrolysis and dehydrocondensation reactions. These processes we can present as following:

Conclusion

Thus, we investigated hydrosilylation reactions of polymethylhydrosiloxane to trialkoxyvinylsilanes in the presence of platinum hydrochloric acid, Karstedt's catalyst and platinum on the carbon (5%) at various ratio of initial compounds were investigated and methylsiloxane oligomers with various amount of alkoxyl side groups were obtained. It was shown that in contrast to platinum hydrochloric acid and Pt/C in case of Karstedt's catalyst hydrosilylation reaction undergoes with ~100% conversion of active ≡Si–H groups. By NMR spectra data it was shown that hydrosilylation reaction mainly proceeds according to anti-Markovnikov rule. Methylsiloxane oligomers with pendant alkoxyl groups are interesting products as silicon hard coatings.

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