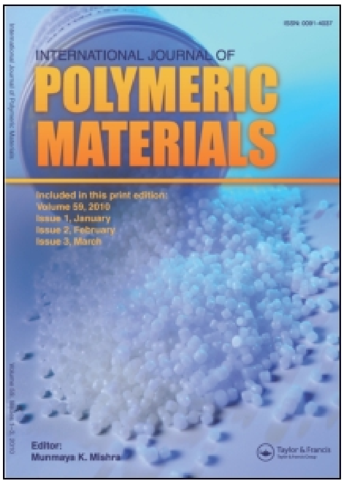
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Comb-type Organosilicon Compounds with Epoxy Groups in the Side Chain

O. Mukbaniani[a][b]; U. Scherf[c]; G. Gurgenidze[a]; M. Karchkhadze[a]; S. Meladze[a]; L. Khananashvili[a]
[a] Javakhishvili Tbilisi State University, Tbilisi, Georgia [b] Sukhumi State University, Branch of Tbilisi State University, Tbilisi, Georgia [c] Max-Planck-Institute in Polymer Research, Mainz

To cite this Article Mukbaniani, O. , Scherf, U. , Gurgenidze, G. , Karchkhadze, M. , Meladze, S. and Khananashvili, L.(2001) 'Comb-type Organosilicon Compounds with Epoxy Groups in the Side Chain', International Journal of Polymeric Materials, 48: 3, 267 — 293

To link to this Article: DOI: 10.1080/00914030108050786

URL: http://dx.doi.org/10.1080/00914030108050786

PLEASE SCROLL DOWN FOR ARTICLE

```
Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or
systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or
distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents
will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses
should be independently verified with primary sources. The publisher shall not be liable for any loss,
actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly
or indirectly in connection with or arising out of the use of this material.
```

Intern. J. Polymeric Mater., 2001, Vol. 48, pp. 267-293
Reprints available directly from the publisher
Photocopying permitted by license only

© 2001 OPA (Overseas Publishers Association) N.V.
Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Comb-type Organosilicon Compounds with Epoxy Groups in the Side Chain

O. MUKBANIANI[a, b, *], U. SCHERF[c], G. GURGENIDZE[a],
M. KARCHKHADZE[a], S. MELADZE[a] and L. KHANANASHVILI[a]

[a]*Javakhishvili Tbilisi State University, 1, I. Chavchavadze ave.,*
380028, Tbilisi, Georgia;
[b]*Sukhumi State University, Branch of Tbilisi State University, Djikia Str. 12,*
Tbilisi, 380087, Georgia;
[c]*Max-Planck-Institute in Polymer Research, Ackermannweg 10, D-55128 Mainz*

(Received 7 October 1999; In final form 7 November 1999)

The reaction of hydride addition of α,ω-bis(trimethylsiloxy)methylhydridesiloxanes with allyl glycidyl ether in the presence of platinum chlorohydric acid and Pt/C at the 1 : 30 ratio of initial compounds has been studied. It was established that when the reaction proceeds without solvent, three-dimensional systems are obtained.

The optimal condition of hydride addition reaction, concentration of the solution, the reaction temperature have been determined. The reaction order, activation energy and hydride addition rate constants were found. In the case of platinum chlorohydric acid hydride addition proceeds with inductive period, and faster than in the case of the catalyst platinum on the carbon Pt/C.

The reactions of primary and secondary amines with epoxy groups containing organosiloxanes were carried out and comb-type organosiloxanes with aminohydroxy groups in the side chain have been obtained. After protonation of amino nitrogen groups in the side chain water soluble organosiloxane oligomers were obtained.

The structure of all synthesized comb-type organosiloxanes were determined by IR, ^{1}H and ^{13}C NMR spectra data.

Keywords: Epoxy organosiloxane; Hydride addition; Platinum chlorohydric acid

Downloaded At: 10:29 19 January 2011

---

*Corresponding author.

Downloaded At: 10:29 19 January 2011

INTRODUCTION

Epoxy containing organosiloxane may be obtained by hydride addition of mono- and dihydride containing linear organosilanes and siloxanes to allyl glycidyl ether [1–4] in the presence of platinium chlorohydric acid in anhydrous isopropanol. During the hydrosililation of allyl glycidyl ether with 1,4-bis(dimethylsilyl) benzene, or diphenylsilane in isothermic condition by calorimetric method at various concentrations of initial compounds and catalyst the hydrosililation rate constants and reaction order have been calculated [5].

Epoxy containing organosiloxanes (with Si—C bonds) are obtained by oxidative epoxidation of α,ω-divinylorganosiloxanes. In this case the yield of synthesised diepoxyorganosiloxanes is about ~85% in tetrachlorocarbon [6].

Epoxy organosiloxanes with various chain lengths may be obtained by anionic cooligomarization of organocyclosiloxanes with 1,3-bis(3-glycidoxypropyl)tetramethyldisiloxane [7].

The epoxy ring-opening reaction with organic amines [8] and organic acids [8, 9] showed that it proceeds with the formation of β and α-aducts. The epoxy ring-opening reactions with primary and secondary amines, showed that in case of primary amines the reaction proceeds completely and has a macromolecular character [10].

Another side increases the probability of some modification reactions of methyl(ethyl)hydrogensiloxanes [11].

EXPERIMENTAL PART

The starting materials for the synthesis of comb-type organosiloxanes with epoxy groups in the side chain were α,ω-bis(trimethylsiloxy)-methylhydridesiloxanes with various degrees of polymerization $n \approx$ 30,53, and allylglycidyl ether.

The organic solvents were purified by drying and distillation. The purity of the starting compounds was controlled by gas–liquid chromatography "ЛХМ-8 МД", phase SKTF-100(10%), the NAW chromosorb, carrier gas He, the 2 M column.

IR spectra of all samples have been taken on an UR-20 instrument, while the ^{1}H NMR spectra on a Perkin-Elmer instrument operating at frequency of 250 MHz. All spectra were obtained with the use of $CDCl_3$ or D_2O as solvent and internal standard.

Gel permeation chromatography was carried out using a Waters Model 6000A chromatograph with an R-401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastyragel columns. Sample concentrations were approximately 3% by weight in toluene, and typical injection volume for the siloxane was 5 μL. Standardization of the GPC was accomplished by the use of styrene or PDMS standards with known molecular weight.

Hydride Addition of Methylhydridesiloxane to Allyl Glycidyl Ether

The hydrosilylation reaction was carried out in a three-necked flask equipped with stirrer and reflux condenser, and calcium chloride drying tube. The initial reagents were placed in the flask and thermostated in an oil bath until constant temperature was achieved. 0,1 M solution of platinum chlorohydric acid in tetrahydrofurane ($5 \div 10 \times 10^{-5}$ g per 1 g of the starting substance) was used as a catalyst. The reaction was performed in an argon atmosphere in the presence of toluene at temperature region of $85 \div 95$°C. Then the reaction mixture was connected to the vacuum and the toluene and unreacted allyl glycidyl ether were removed. The oligomers I-II were isolated after the solvent was removed in vacuum at 70-80°C. They are clear transparent oils. The other epoxy-organosiloxane II was obtained by the same method.

Addition of Butylamine to Epoxyorganosiloxane

The reaction was carried out in a three-necked flask equipped with a reflux condenser and calcium chloride tube, dropping funnel and mechanical stirrer. A solution of 2,1370 g (0,3969 mmole) of

Downloaded At: 10:29 19 January 2011

epoxyorganosiloxane in 15 mL of anhydrous toluene and 2,6076 g (0,03572 mole) butylamine was refluxed under argon, until all epoxide resonances at $\delta = 2,7$ and $\delta = 3,1$ ppm disappeared from the ^{1}H NMR spectrum. Then the solvent and excess amine were removed in vacuum at 80°C to give 2,9 g (96%) of the product V.

Addition of Diethylamine to Epoxyorganosiloxane

The reaction was carried out in a three-necked flask equipped with a reflux condenser and chlorocalcium tube, dropping funnel and mechanical stirrer. A solution of 2,5825 g (4,796 mmole) of epoxyorganosiloxane in 17 mL of anhydrous toluene and 3,1509 g (0,043 mole) diethylamine were refluxed under argon, until the disappearance of epoxide resonances at $\delta = 2,7$ and $\delta = 3,1$ ppm in the ^{1}H NMR spectrum. Then the solvent and excess amine were removed in vacuum at 80°C to give 3,5 g (97%) of the product X.

The synthesis of other hydroxyaminosiloxanes were carried out using the same method.

Reaction of Hydrogen Bromide with Diethylaminohydroxyorganosiloxane

The reaction was carried out in a three-necked flask equipped with a reflux condenser and chlorocalcium tube, dropping funnel and mechanical stirrer. To a solution of 0,9828 g (0,1297 mmole) of diethylaminohydroxyepoxysiloxane in 10 ml anhydrous toluene 0,3145 g (3,89 mmole) (48%) HBr was added in 3 ml water at 0°C temperature range. From water solution 1,2 g (93%) transparent vitreous product XIII was received.

Reaction of Acetic Acid with Diethylaminohydroxyorganosiloxane

The reaction was carried out in a three-necked flask equipped with a reflux condenser and calcium chloride tube, dropping funnel and mechanical stirrer. To a solution of 1,7662 g (0,233 mmole) of diethylaminohydroxyepoxysiloxane in 10 ml dry CH_2Cl_2 there were added

Downloaded At: 10:29 19 January 2011

0,4199 g (6,993 mmole) acetic acid (99,8%) in 15 ml water at 0°C temperature range. After that the solution clouded. After workup of the water solution 2,1 g (95,5%) of the compound XV was obtained as a transparent oil.

RESULTS AND DISCUSSION

In the literature there is some information about the synthesis of polyfunctional organosiloxanes containing glycidoxypropyl groups in the side dimethylsiloxane chain [12]. The present paper deals with synthesis and studies of the properties of comb-type organosiloxanes containing epoxy groups in the side chain.

For the purpose of synthesis of organosiloxanes with epoxy group in the side chain the reaction of hydride addition of α,ω-bis(trimethylsiloxy)methylhydridesiloxanes ($n \approx 30,53$) to allyl glycidyl ether at 1:30 or 1:53 ratio of initial compounds, in the presence of platinum chlorohydric acid or Pt/C as a catalyst has been investigated.

The reaction of hydrosilylation was investigated without solvent in the presense of catalysts at temperature range 80–90°C. In both cases the hydrosilylation proceeds with an inductive period, after that the reaction proceeds autocatalitically with the formation of three-dimensional systems.

For the purpose of synthesis of soluble, epoxy group containing comb-type organosiloxanes, hydrosilylation reactions were investigated in dilute solutions of anhydrous toluene. The optimal concentration is about 0,1 mole/l. At concentrations lower than this, the processes do not take place. The hydrosilylation was carried out at various temperatures $80 \div 90$°C. The course of the reaction was observed by the decrease of amount of active Si—H groups. As it is clear from Figure 1 with the rise of the temperature the rate of hydride addition increases. At a fixed temperature the rate of hydrosilylation in the presence of platinum chlorohydric acid is higher than in case of platinum on carbon. As it is obvious from Figure 1 the reaction proceeds vigorously mainly during the first hours. After 2 h the conversion slowly changes.

Downloaded At: 10:29 19 January 2011

Downloaded At: 10:29 19 January 2011

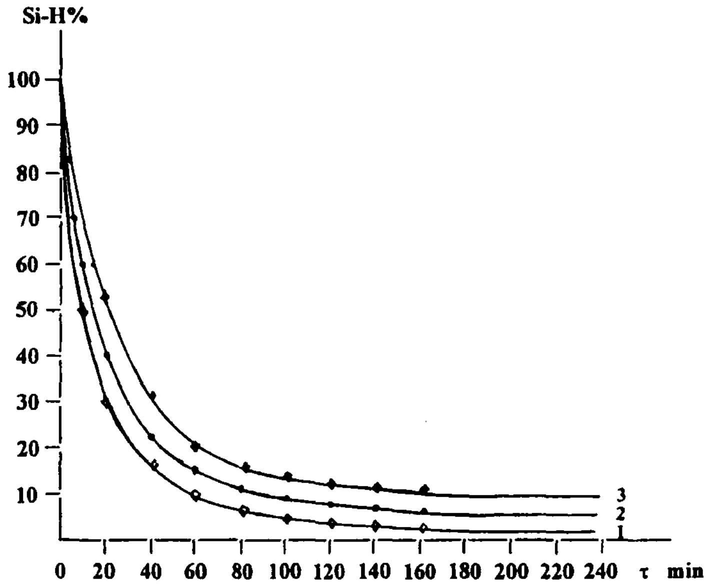


FIGURE 1 Dependence of changes of active Si—H% groups on time upon hydride addition of allyl glycidyl ether to α,ω-bis(trimethylsiloxy)methylhydridesiloxane, where curve 1 is at 90°C, curve 2 is at 85°C and curve 3 is at 80°C.

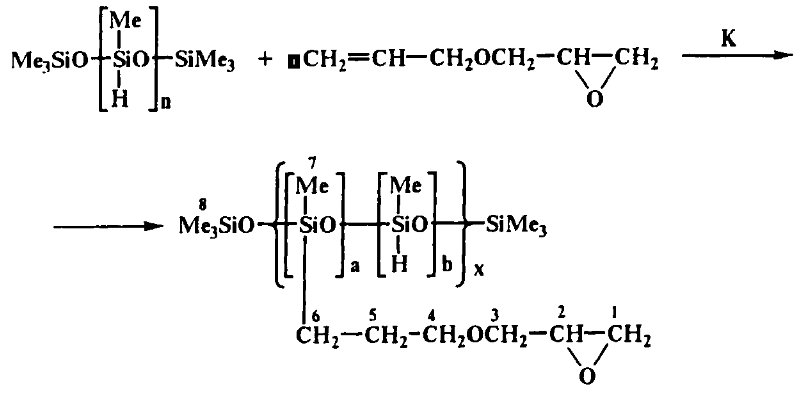
From Figure 1 we can see that the conversion of active Si—H groups is not complete and decreases from 98% ($t = 90°C$) to 92% ($t = 80°C$).

The synthesised oligomers with epoxy groups in the side chain, after removal of solvents are colourless (or light yellow) liquid transparent products well soluble in ordinary organic solvents, with $\eta_{sp} \approx 0{,}04 \div 0{,}08$.

The IR spectra of the oligomers revealed that the absorption bands characteristic of Si—H bonds in the range 2160–2170 cm^{-1} do not vanish completely. In the IR spectra one can see the absorption bands at 850, 920 and 4545–4550 cm^{-1} characteristic for epoxy groups, the absorption bands at 1020–1100 and 1150 cm^{-1} corresponds to asymmetric valence oscillation for the linear Si—O—Si and C—O—C simple ether bonds, as well as absorption bands in the range 2900–2950 cm^{-1}, typical for valence oscillations of the CH bonds in the CH_2 groups in the ethylenic bridges and absorption bands at 1270 cm^{-1} characteristic for Si—Me bonds. Hydrosilylation reaction proceeds according to the following

Downloaded At: 10:29 19 January 2011

scheme:



1

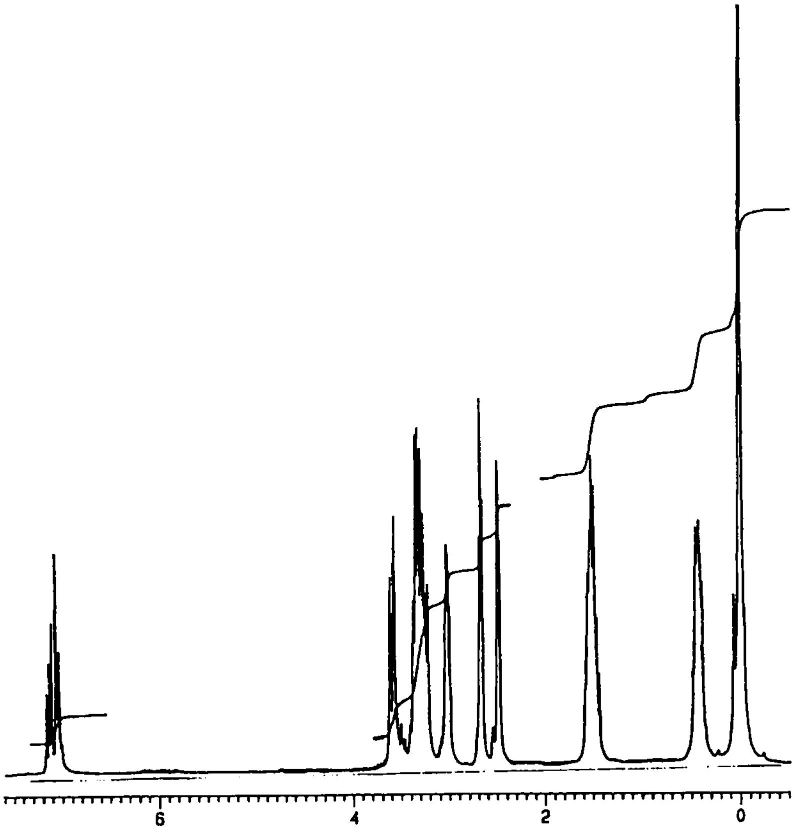


FIGURE 2 ^{1}H NMR spectra of oligomer III.

Downloaded At: 10:29 19 January 2011

where:

$$(a+b)x = n \quad n \approx 30, 53$$

$n = 30$, I – (80°C); II – (85°C); III – (90°C); $-H_2PtCl_6$
$n = 53$, IV – (85°C); $-H_2PtCl_6$
$n = 30$, II′ – (85°C); –Pt/C

In the ^1H NMR spectra of oligomer III, Figure 2, one can observe the singlet signals for methyl protons in trimethylsiloxy group with

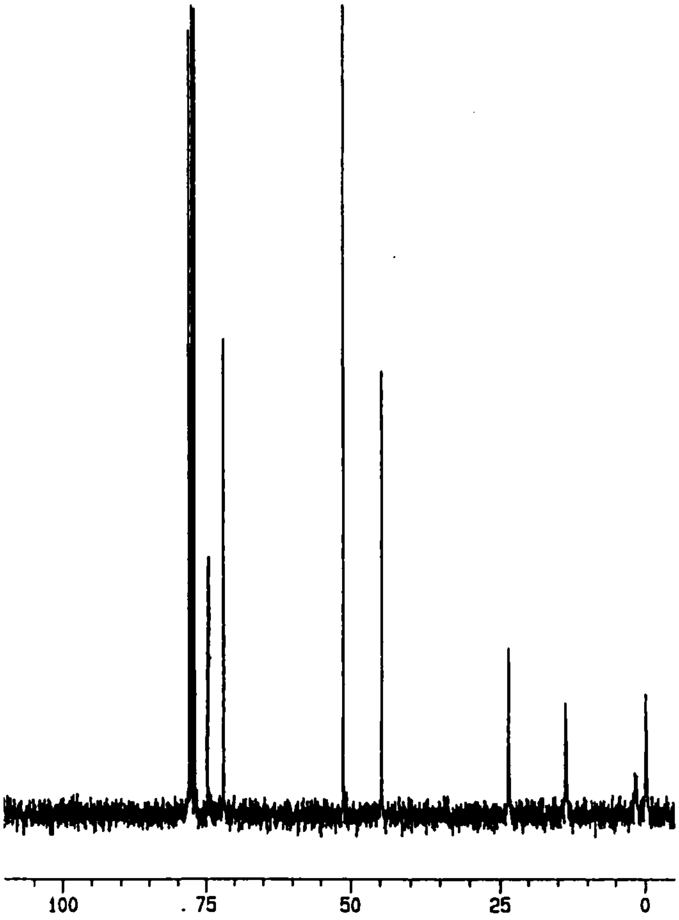


FIGURE 3 ^{13}C NMR spectra of oligomer III.

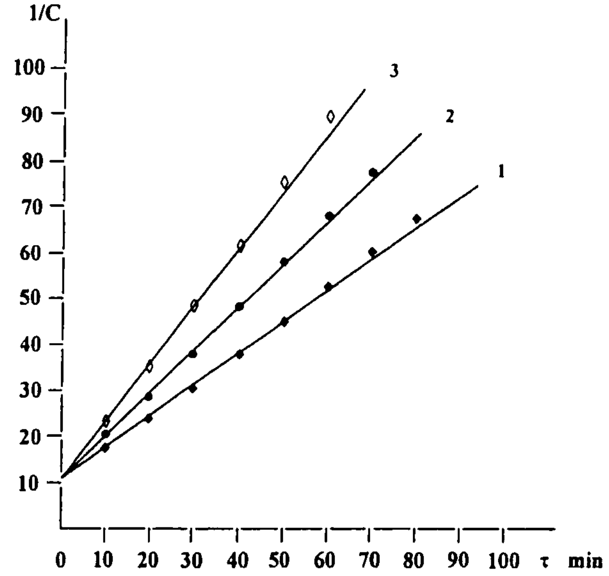


FIGURE 4 Dependence of reverse concentration on the time, where curve 1 is at 80°C, curve 2 at 85°C and curve 3 is at 90°C.

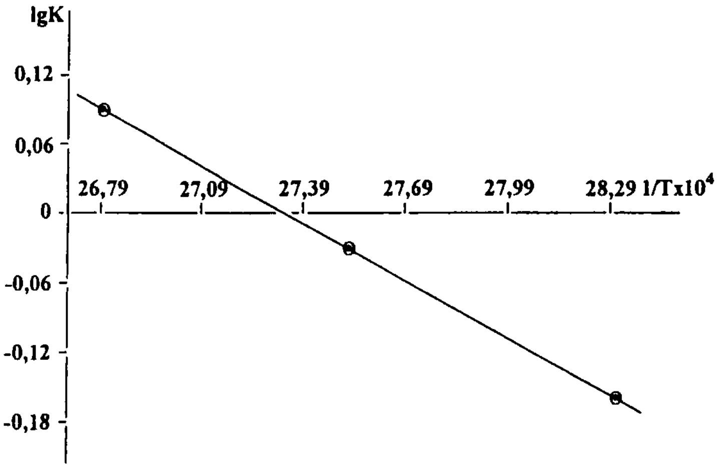


FIGURE 5 Dependence of reverse temperature on the rate constants of upon hydride addition of allyl glycidyl ether to α,ω-bis(trimethylsiloxy)methylhydridesiloxane.

chemical shift $\delta = 0{,}05$ ppm, for methyl group at $\delta = 0{,}01$ ppm, 0,47 ppm (s-C^6H_2), 1,50 ppm (s-C^5H_2), 3,20; 3,30; 3,45; 3,50 ppm (m-C^3H_2, C^4H_2); 3,0 ppm (s-C^2H) and 2,41 and 2,65 ppm (d-C^1H_2).

Downloaded At: 10:29 19 January 2011

Downloaded At: 10:29 19 January 2011

TABLE I Some physical–chemical properties of methylhydridesiloxanes with organic branching side groups

No.	Yield, %	η_{sp}*	d_1, Å	$\overline{M}_w$	Elementary composition, % C	H	Si	N	Br/S
I	92	0,05	–	$\frac{5384}{5200}$	$\frac{48,13}{47,74}$	$\frac{8,19}{8,01}$	$\frac{16,77}{16,30}$	–	–
II	94	0,04	–	–	$\frac{48,13}{47,98}$	$\frac{8,19}{8,08}$	$\frac{16,77}{16,45}$	–	–
II′	92	0,04	–	–	$\frac{48,13}{47,72}$	$\frac{8,19}{7,93}$	$\frac{16,77}{16,56}$	–	–
III	97	0,05	–	–	$\frac{48,13}{48,01}$	$\frac{8,19}{8,21}$	$\frac{16,77}{16,14}$	–	–
IV	93	0,06	–	$\frac{9384}{9000}$	$\frac{48,13}{48,81}$	$\frac{8,19}{7,87}$	$\frac{16,77}{16,60}$	–	–
V	97	0,06	–	$\frac{7576}{7500}$	$\frac{53,21}{53,30}$	$\frac{10,21}{10,13}$	$\frac{11,85}{11,60}$	$\frac{5,54}{5,12}$	–
VI	97	0,07	–	$\frac{8596}{8600}$	$\frac{59,46}{59,13}$	$\frac{8,29}{7,87}$	$\frac{10,44}{10,13}$	$\frac{4,88}{4,41}$	–
VII	98	0,06	–	$\frac{9016}{8900}$	$\frac{60,68}{60,31}$	$\frac{8,58}{8,30}$	$\frac{9,96}{9,63}$	$\frac{4,66}{4,20}$	–
VIII	–	–	–	$\frac{9134}{8700}$	$\frac{52,02}{51,76}$	$\frac{7,09}{6,70}$	$\frac{9,80}{9,31}$	$\frac{4,59}{4,70}$	$\frac{10,51}{9,78}$
IX	97	–	–	$\frac{8654}{8300}$	$\frac{54,91}{54,28}$	$\frac{7,48}{6,97}$	$\frac{10,35}{9,86}$	$\frac{4,85}{4,41}$	–
X	98	0,07	6,94	$\frac{7576}{7600}$	$\frac{53,21}{52,78}$	$\frac{10,21}{9,89}$	$\frac{11,85}{11,56}$	$\frac{5,54}{5,08}$	–
XI	97	0,07	6,94	$\frac{8596}{8500}$	$\frac{59,46}{59,22}$	$\frac{8,29}{8,45}$	$\frac{10,44}{10,20}$	$\frac{4,88}{4,61}$	–

Downloaded At: 10:29 19 January 2011

XII	98	0,06	6,90	$\frac{9258}{9100}$	$\frac{59,10}{58,76}$	$\frac{10,96}{10,57}$	$\frac{9,70}{9,34}$	$\frac{4,53}{4,23}$	–
XIII	98	0,08	–	$\frac{11026}{10900}$	$\frac{46,36}{46,12}$	$\frac{6,69}{6,45}$	$\frac{8,12}{8,33}$	$\frac{3,80}{3,54}$	$\frac{21,76}{20,89}$
XIV	98	0,08	7,08	$\frac{10006}{9900}$	$\frac{40,29}{40,02}$	$\frac{7,97}{7,55}$	$\frac{8,95}{8,76}$	$\frac{4,19}{3,80}$	$\frac{23,98}{23,40}$
XV	97	0,08	7,02	$\frac{9436}{9400}$	$\frac{50,35}{50,11}$	$\frac{9,40}{9,16}$	$\frac{9,49}{9,13}$	$\frac{4,45}{4,09}$	–

•In 1% toluene solution (XIV and XV in water) at 25°C.
In numerator there are calculated values, in denominator experimental values.
Average molecular weights were determined by gel permeation chromatographic method.

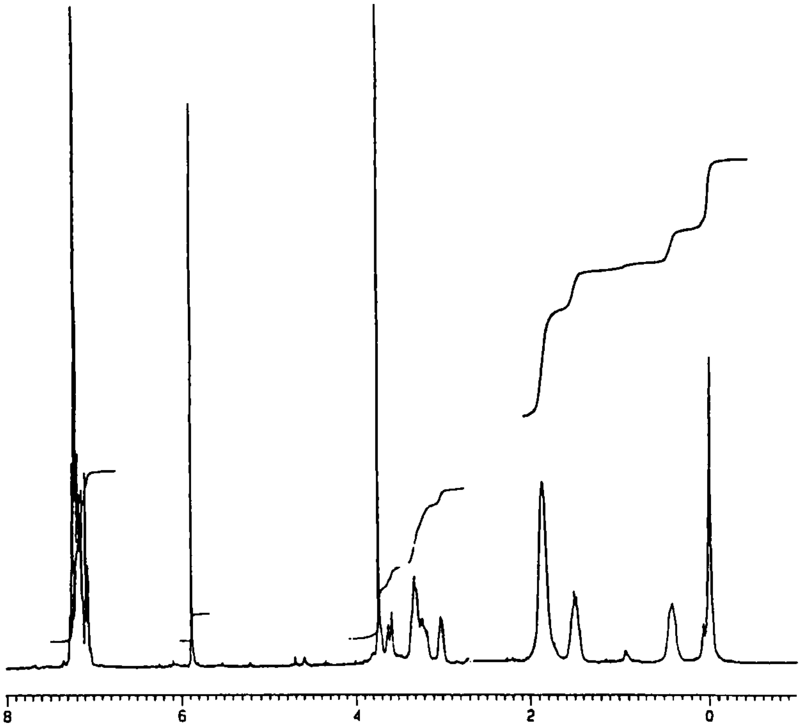


FIGURE 6 ^{1}H NMR spectra of oligomer VI.

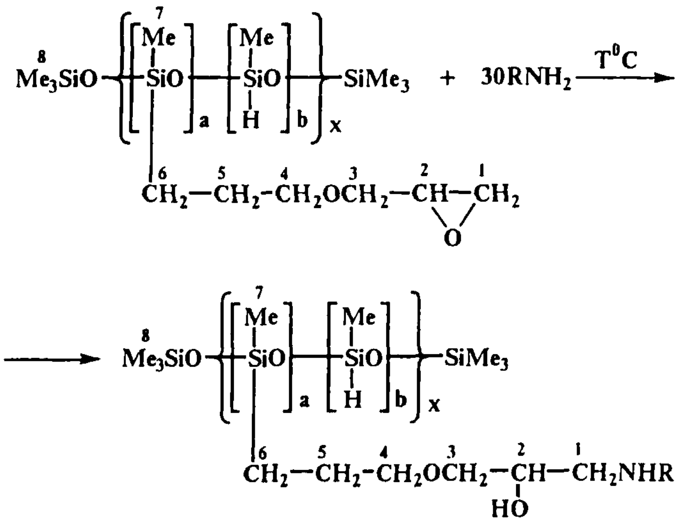
In the ^{13}C NMR spectrum of oligomer III, Figure 3, one can observe the signals at 1,85 ppm (C^7); 13,9 ppm (C^6); 23,56 ppm (C^5); 71,86 ppm (C^4); 74,43 ppm (C^3); 51,29 ppm (C^2) and 44,70 ppm (C^1).

Figure 4 shows the time dependence of the reverse concentration, from which it is evident, that at the beginning stages the hydrosilylation reaction is of second order. This result is in opposition with literature data [5], where the authors proved that depending on the original concentration of reacting compounds the hydrosilylation reaction may be of first order at low value of concentration, or zero order at higher concentration.

From Figure 4 the hydrosilylation rate constants at various temperatures were calculated: $K_{85°C} = 0,6878$, $K_{90°C} = 0,9325$ and $K_{95°C} = 1,2571$. There was found that for each increase in temperature of 10°C the reaction rate constants increase approximately 1,35 times.

Downloaded At: 10:29 19 January 2011

Figure 5 shows the dependence of logarithm of hydrosilylation rate constants on the reverse temperature, from which the activation energy was calculated $E_{\mathrm{activ}} \approx 30{,}6$ kJ/mole. Comb-type organosiloxanes with epoxy groups in the side chain reacted with primary amines. During the epoxy ring-opening reaction in the melt, the reaction proceeds with the formation of three-dimensional systems, this fact may be explained by the ring-opening reaction in the presence of reactionable secondary (—NH—) groups, which enter the ring-opening intra- and intermolecular condensation. In order to receive soluble comb-type hydrophilic hydroxy and amino groups pendant to the hydrophobic methylsiloxane chain, the reaction of epoxyorganosiloxanes with primary amines were carried out in 10% solution of anhydrous toluene. The reaction products were heated up to the boiling point of toluene for 12 hours. The completeness of the reaction was confirmed by ^{1}H NMR spectra by the disappearance of the resonance signals characteristic for epoxy groups. As is seen from Table I aminohydroxysiloxanes were obtained in good yields. The reaction proceeds according to the following scheme:



2

where $(a+b)x=30$. R = C_4H_9 (V), $C_6H_5CH_2$ (VI), 2,3-$Me_2C_6H_3$ (VII), 1,4-HOC_6H_4 (VIII), o-HSC_6H_4 (IX).

Downloaded At: 10:29 19 January 2011

The synthesized secondary aminohydroxysiloxanes (V, VI, VII and IX) are colorless or slightly yellow compounds soluble in ordinary organic solvents. Unfortunately, all attempts to obtain the soluble product VIII failed. It is possible that during the reaction of *p*-aminophenol with epoxymethylhydridesiloxanes secondary intra- and intermolecular reactions take place. The composition and structure of the synthesized compounds were determined by element analysis, by finding the molecular masses, and by IR and NMR spectra data.

In the ^{1}H NMR spectra of all secondary aminohydroxymethylhydridesiloxanes one can observe the singlet signals with chemical shifts at 0,1–0,15 ppm for methyl protons at silicon (7 and 8 position), $\delta = 0,5$ ppm (C^6H_2); $\delta = 1,5$ ppm (C^5H_2); $\delta = 1,9 \div 2,1$ ppm

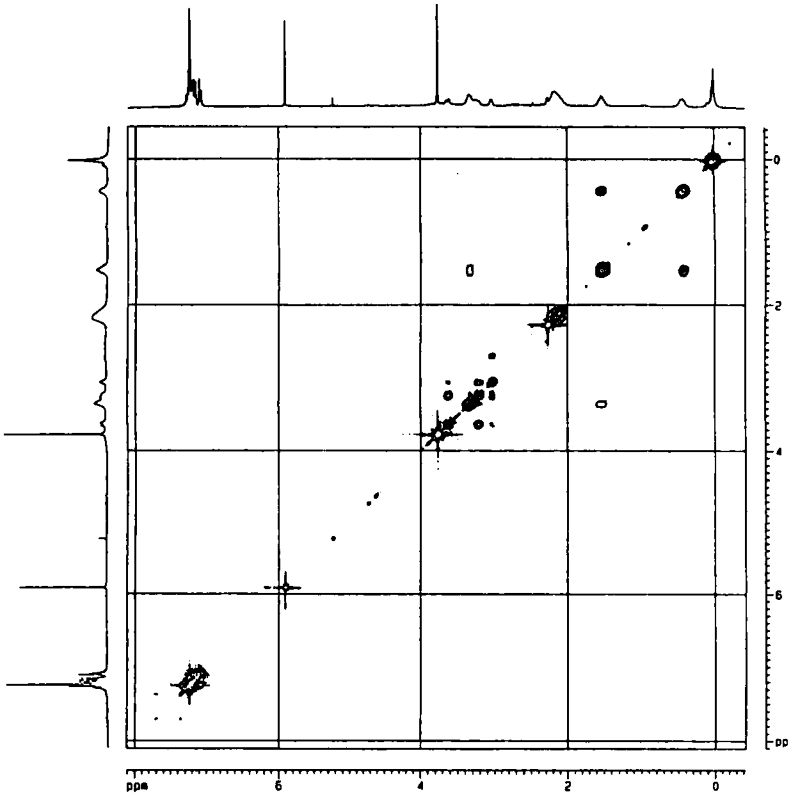


FIGURE 7 COSY NMR spectra of oligomer VI.

Downloaded At: 10:29 19 January 2011

Downloaded At: 10:29 19 January 2011

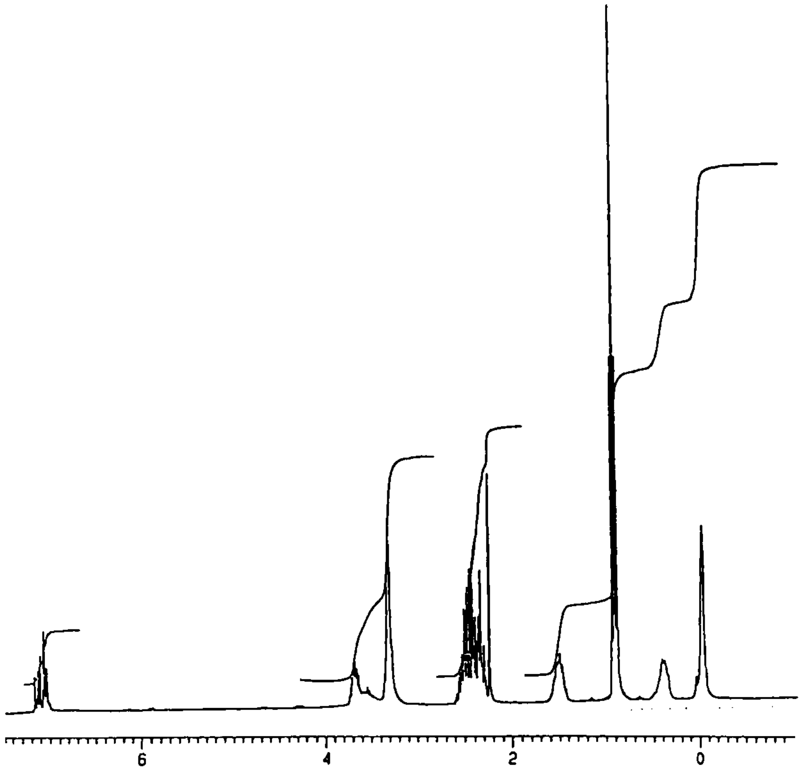


FIGURE 8 ^{1}H NMR spectra of oligomer X.

(NH); $\delta =$ 2,9 ÷ 3,0 ppm (C^4H_2); $\delta = 3{,}2$ ppm (C^3H_2); $\delta = 3{,}3$ ppm (C^2H); $\delta =$ 3,6 ppm (C^1H_2); $\delta = 3{,}7 - 3{,}8$ ppm (OH) (see Fig. 6 for compound VI).

In the ^{1}H NMR spectra of compound IX one can see broadened singlet signal which may correspond to labile protons linked to electronegative nitrogen and sulfur groups. By integral intensity this signal corresponds approximately to two proton absorption intensity, but this does not exclude the existence of SiH groups, because a proton exchange reaction is possible which may be seen from broadened singlet signals. That is why in compound IX the existence of NH_2 or NH and SH groups is possible.

Full identification of amino-hydroxymethylsiloxanes was achieved for example from benzylaminohydroxysiloxane VI by using COSY

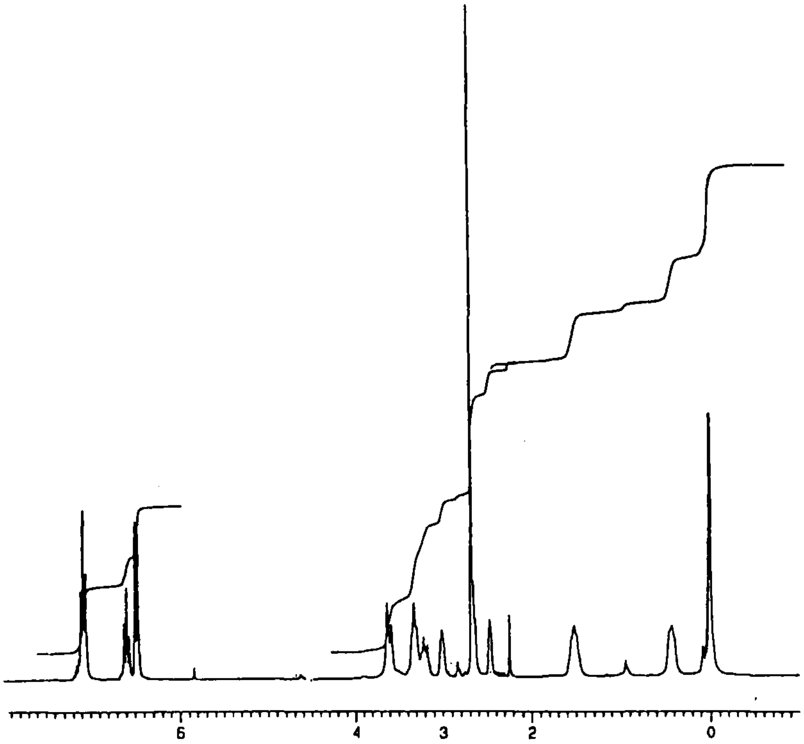


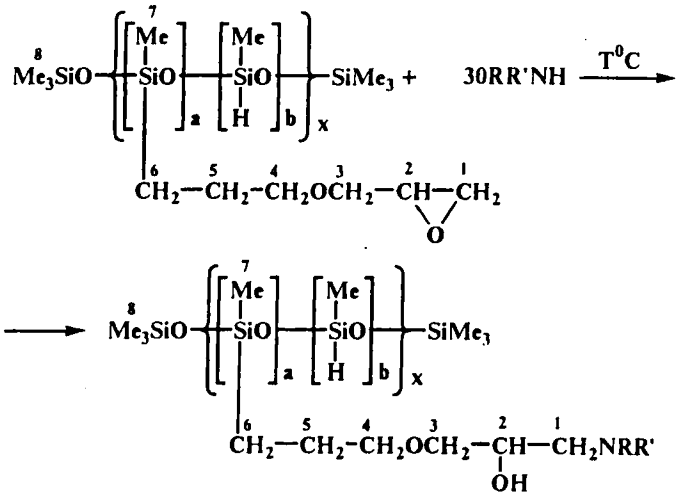
FIGURE 9 ^1H NMR spectra of oligomer XI.

Downloaded At: 10:29 19 January 2011

NMR spectra. In Figure 7 one can see the resonance signals in two dimensions. Where the resonance signals at $\delta \approx 0,1$ corresponds to methyl groups at 7 and 8 positions. The resonance signals with chemical shift at δ 0,5; 1,5 and 2,2 correspond to methylene groups in 7,8; 6 and 5 positions and resonance signal with chemical shift in the range $\delta \approx 7,0 \div 7,4$ ppm corresponds to phenyl protons.

In the IR spectra of all aminohydroxymethylsiloxanes one can see the absence of absorption bands characteristic for epoxy bonds at 910 cm^{-1} and absorption bands characteristic for —NH— and —OH bonds at 3400–3600 cm^{-1} (those absorption bands appear on top of each other). Hence it follows that all epoxy groups take place in ring-opening reaction. There the absorption bands for trimethylsiloxy are observed, Si—Me, SiOSi and COC bonds at 840, 1275, 1000–1130 cm^{-1} respectively.

Comb-type organosiloxanes with epoxy groups in the side chain were reacted with secondary amines. The reaction was carried out in 10% solution of anhydrous toluene. The reaction products were heated up to the boiling point of toluene for 12 hours. The completion of the reaction was confirmed from ^{1}H NMR spectra by the disappearance of the resonance signals characteristic for epoxy groups. As is seen from Table I the yields of comb-type aminohydroxysiloxanes are higher because this reaction proceeds without any complication, according to the following scheme:



2

where $(a+b)x=30$. $R=R'=C_2H_5$ (X), $R=Me$, $R'=C_6H_5$ (XI), $R=R'=C_4H_9$ (XII).

The composition and structure of tertiary aminohydroxysiloxanes was established by means of element analysis, by finding the molecular masses, and by IR and NMR spectra data. In ^{1}H NMR spectra of compounds X ÷ XII one can observe resonance signals with chemical shifts 0,1–0,15 ppm for methyl protons at silicon (in 7 and 8 position), $\delta=0,5\div0,6$ ppm (C^6H_2); additionally complicated signals with chemical shift $\delta=0,9\div1,1$ ppm for methyl protons in

Downloaded At: 10:29 19 January 2011

alkaline fragment (compounds X and XII); $\delta = 1{,}5 \div 1{,}6$ ppm (C^5H_2); $\delta = 2{,}3 \div 2{,}7$ ppm (NC^1H_2 and NCH_2); $\delta = 2{,}9 \div 3{,}0$ ppm (C^4H_2); $\delta = 3{,}2$ ppm (C^3H_2); $\delta = 3{,}3$ ppm (C^2H); $\delta = 3{,}6$ ppm (C^1H_2); $\delta = 3{,}7$ ppm (OH) and $\delta = 4{,}2$ ppm (Si—H) (see Figs. 8 and 9 for compound $X \div XII$). Full identification of tertiary aminohydroxymethylsiloxanes was achieved for example of benzylaminohydroxysiloxane X by using COSY NMR spectra. In the ^{13}C NMR spectra of compound X, Figure 10, one can see the signals for carbon attached to hydroxyl groups at $\delta = 67{,}13$ ppm and signals for carbon attached to nitrogen at δ 47,57 and δ 56,50 ppm. Figure 11 one can see the resonance signals in two dimensions. Where the resonance 1 at $\sim 0{,}1$

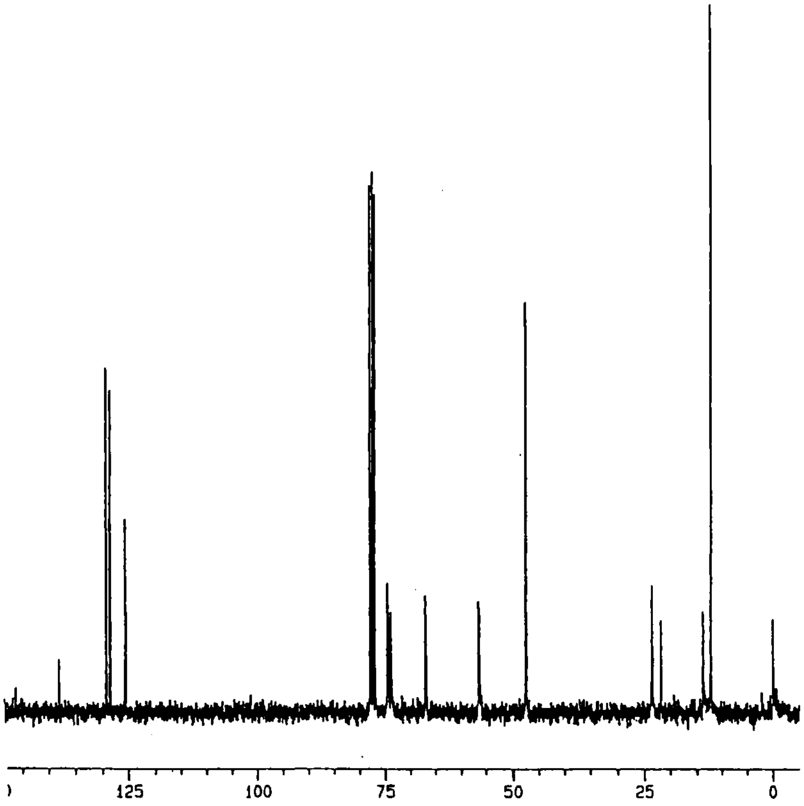


FIGURE 10 ^{13}C NMR spectra of oligomer X.

Downloaded At: 10:29 19 January 2011

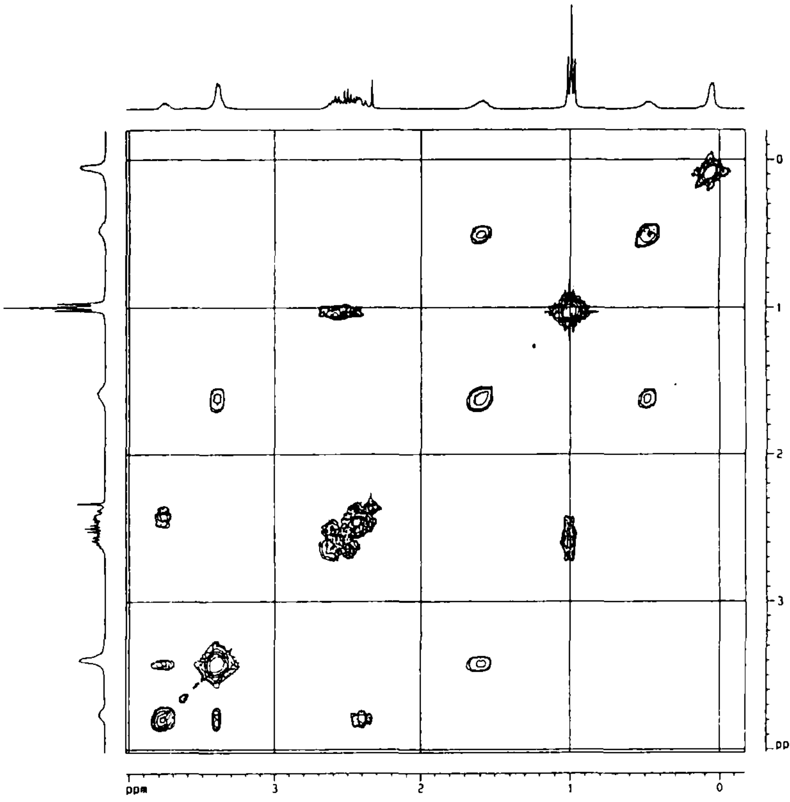


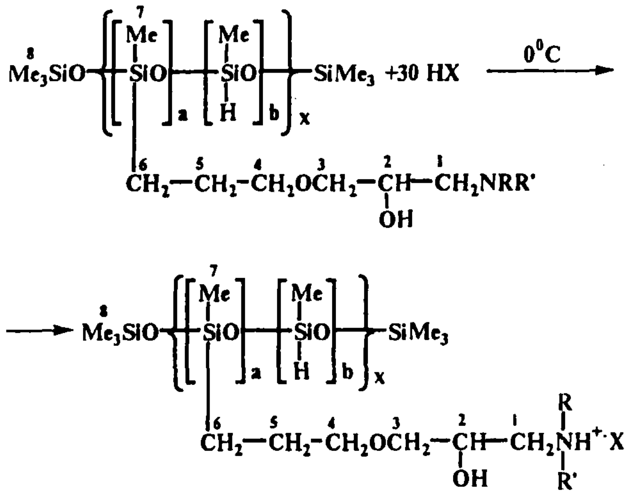
FIGURE 11 COSY NMR spectra of oligomer X.

Downloaded At: 10:29 19 January 2011

corresponds to methyl groups at 7 and 8 positions. The resonance signal at δ 0,5; 1,5 and 3,4 corresponds to methylene groups in 6, 5 and 4 positions. The triplet signal in the range $\delta = 0{,}9 \div 1{,}1$ ppm corresponds to methyl groups in ethyl fragment. In the IR spectra of tertiary aminohydroxysiloxanes X ÷ XII one can see narrow absorbtion bands characteristic for secondary hydroxy group at $3600\,\mathrm{cm}^{-1}$, from which it is evident that the reaction of amines with epoxyorganosiloxanes mainly proceeds with the formation of α-aduct. The tertiary amines did not react with epoxy containing comb-type organosiloxanes because the tertiary amines did not have the active hydrogen groups which may enter the ring-opening reaction.

Downloaded At: 10:29 19 January 2011

For the purpose of synthesis of siliconorganic quartenary ammonium salts, the reaction of hydrogen bromide or acetic acid with aminohydroxyorganosiloxanes has been investigated. It was very interesting to test the stability of siloxane chain and to determine that such strong acid as hydrogen bromide (or acetic acid) can break the linear siloxane chain. The reaction was carried out at 0°C temperature to prevent the break of SiOSi backbone. Hydrogen bromide in equimolar amount was added and stirred for 4 hours. The reaction proceeds according to the following scheme:



where $(a+b)x=30$; X = Br; R = Me, R′ = C_6H_5 (XIII); R = R′ = C_2H_5 (XIV). X = CH_3COO, R = R′ = C_2H_5 (XV).

The synthesized salts are vitreous transparent colorless products. Compounds XIV and XV are soluble in water and compound XIII in organic solvents such as CH_2Cl_2, chloroform, *etc.*, by GPC analysis it was shown that during the reaction of aminohydroxysiloxanes with the above-mentioned acids SiOSi backbone breakdown reactions do not take place (see Tab. I). The compounds XIII–XV were characterized by ^1H, ^{13}C NMR and IR spectra data. As is seen from ^1H NMR spectra of the protonated compounds XIII–XV, Figures 12–15, one can see resonance singlet signals for methyl protons at silicon atom $\delta \approx 0{,}1-0{,}13$ ppm (for hydrogen protons at 8 and 7

Downloaded At: 10:29 19 January 2011

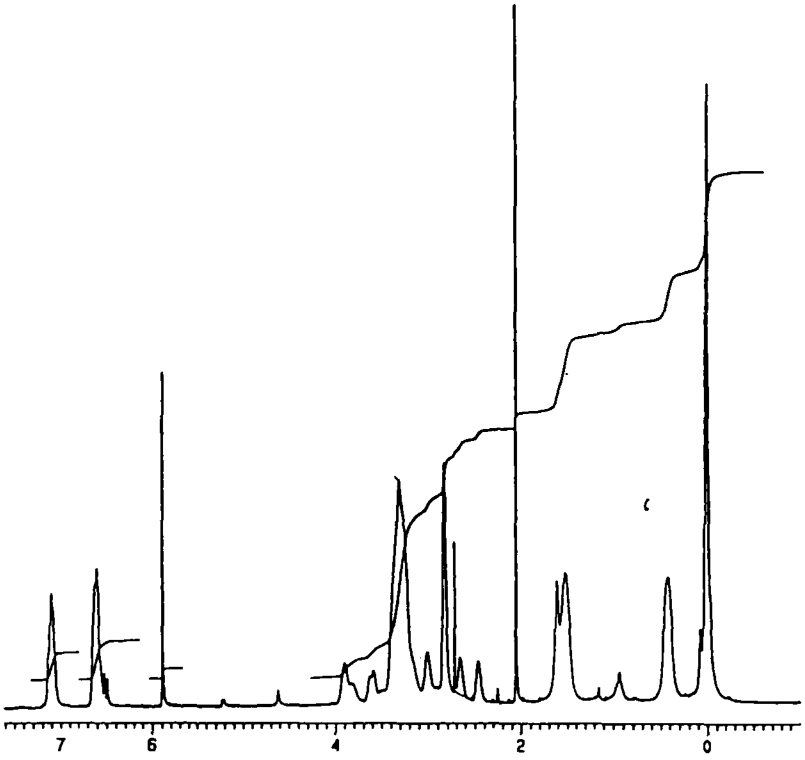


FIGURE 12 ^{1}H NMR spectra of oligomer XIII.

position respectively), for protons in methylene groups with chemical shifts at $\delta \approx 0,5$; 1,5 ppm; in the range 2,9 ÷ 3,6 ppm (6, 5, 4 and 3 position). A comparison of chemical shifts for N—CH$_2$— groups in tertiary and quaternary aminohydroxysiloxanes shows a significant shift to low field for quaternary compounds.

Full identification of protonated aminohydroxymethylhydridesiloxanes by COSY NMR spectra was received for compound XIV (Fig. 16). In 2-dimensional COSY NMR spectra, Figure 16, the resonance signals at $\delta \approx 0,1$ and $\delta \approx 0,13$ ppm correspond to methyl protons at 7 and 8 positions. The resonance broadened signals with chemical shift and with center at $\delta \approx 0,5$; 1,3; 1,7; 3,2 and 3,5 ppm correspond to protons of methylene groups in 6 ÷ 1 positions and in ethyl fragment.

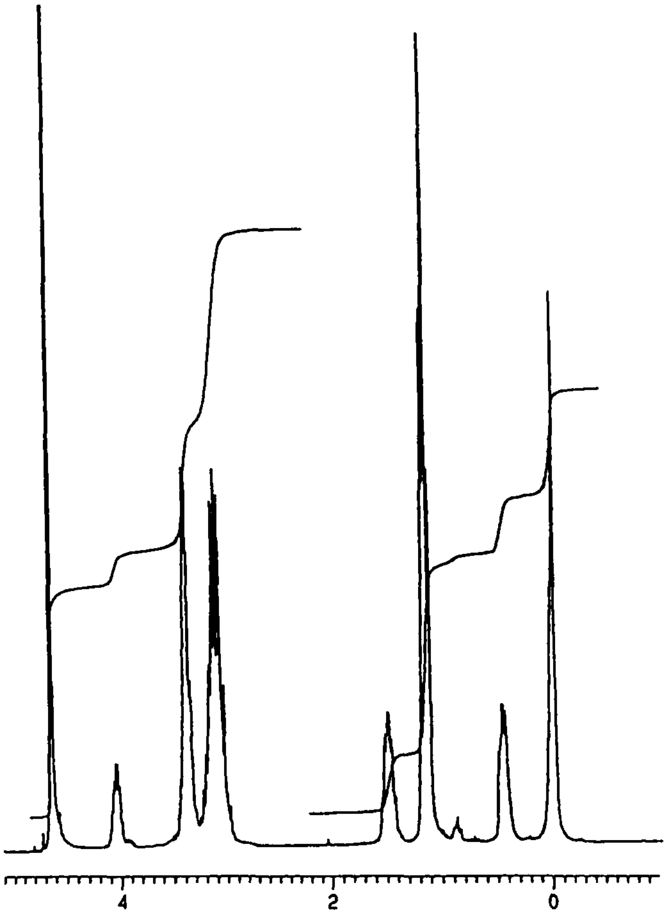


FIGURE 13 ^{1}H NMR spectra of oligomer XIV.

The large IR absorption band in the region 3200–3600 cm^{-1} corresponds to the associated hydroxyl and cationic nitrogen groups. The absorption bands in the region 1590–1650 cm^{-1} correspond to NH_2^+ group.

For some synthesized aminohydroxymethyl(hydride)siloxanes X-ray diffraction studies have been carried out. As is seen from Figure 17 the synthesized methylhydridesiloxane with amino and hydroxy

Downloaded At: 10:29 19 January 2011

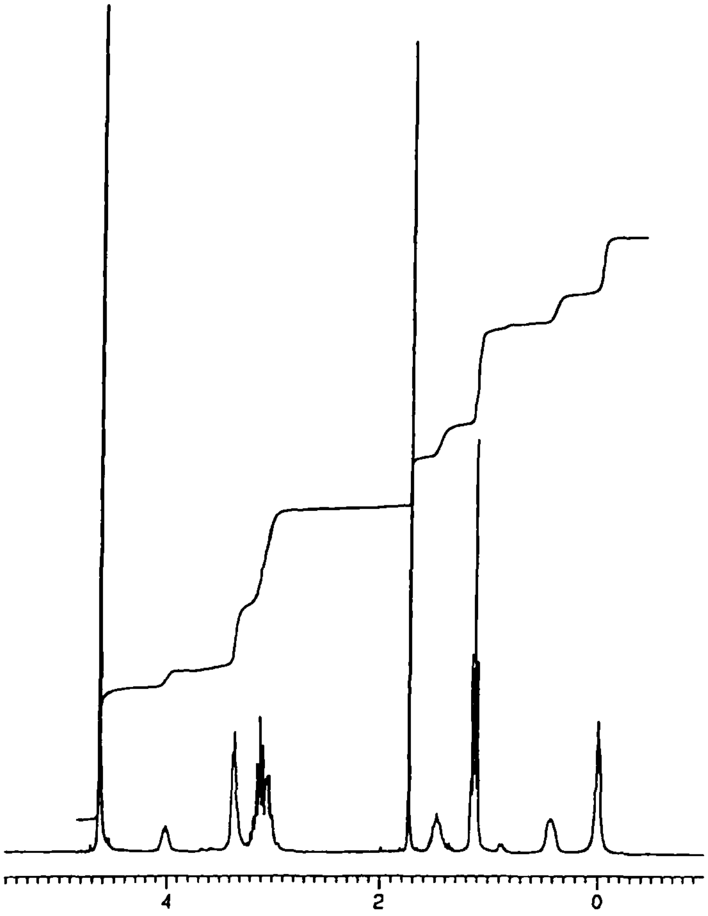


FIGURE 14 ^{1}H NMR spectra of oligomer XV.

groups in the side chain as well as protonated corresponding compounds are amorphous systems. On the diffractograms one can observe two maxima at $2\theta^\circ = 12{,}5^\circ$ and $2\theta = 18{,}0^\circ \div 22{,}0^\circ$. The main maximum $2\theta^\circ = 12{,}5^\circ$ which corresponds to interchain distance, changes from $d_1 = 6{,}94\,\text{Å}$ (for compounds X and XI) up to $d_1 = 7{,}08\,\text{Å}$, these increasing values of interchain distances correspond to protonated aminohydroxymethylhydridesiloxane XIV.

Downloaded At: 10:29 19 January 2011

Downloaded At: 10:29 19 January 2011

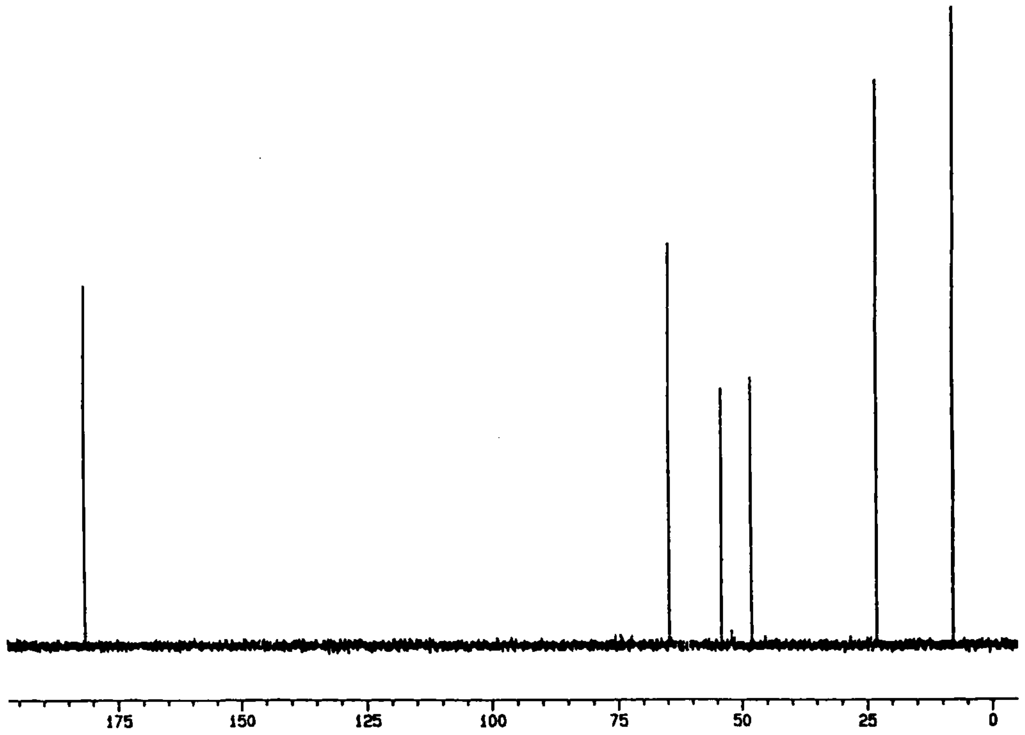


FIGURE 15 ^{13}C NMR spectra of oligomer XV.

Downloaded At: 10:29 19 January 2011

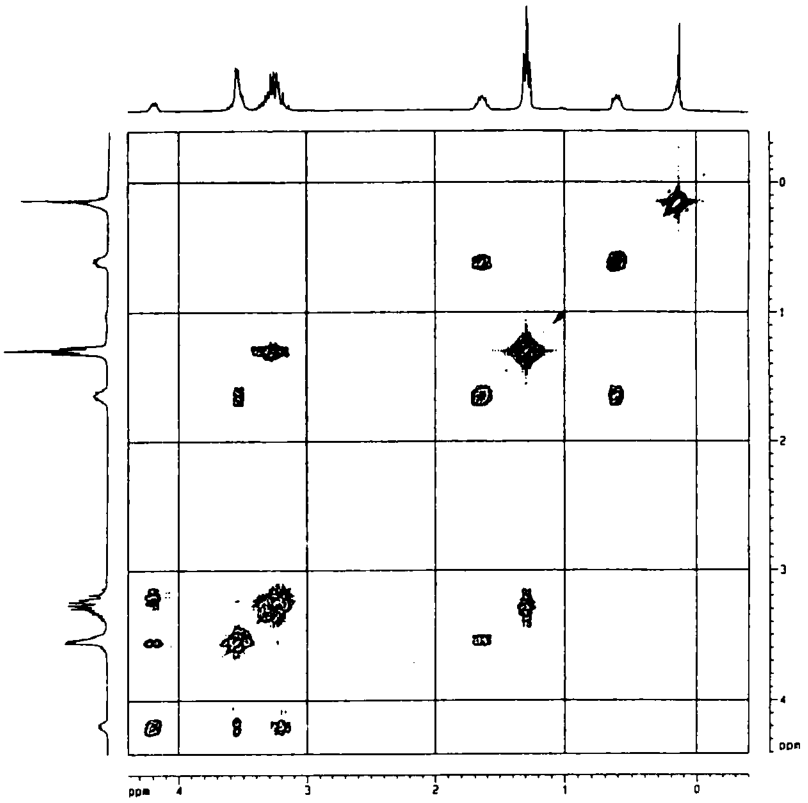


FIGURE 16 COSY NMR spectra of oligomer XIV.

A thermogravimetric investigation of some synthesized compounds in isothermic condition (200°C) was carried out. As is seen from Figure 18 (curves 1 and 2), for aminohydroxysiloxanes X and XI mass losses for 10 h do not exceed 21–24%, while for the protonated compound XIV for first 3 h the mass losses reach about 74% (Fig. 18, curve 3), after which the destruction process proceeds slowly.

So, methylhydridesiloxanes with hydroxy and amino functional groups in the side chain were synthesized by us for the first time, and by protonation of aminohydroxysiloxanes the protonated aminohydroxysiloxanes were obtained.

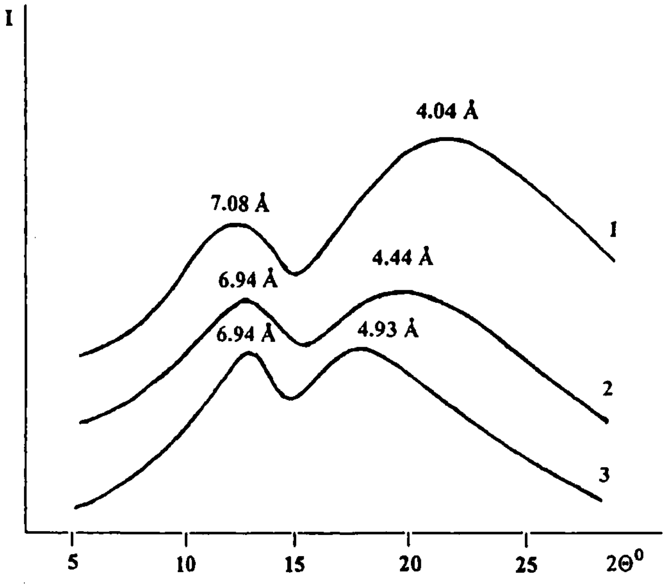


FIGURE 17 Diffractograms of comb-type organosiloxanes with aminohydroxy groups in the side chain. Where curve I corresponds to oligomer XIV, curve 2-XI and curve 3-X.

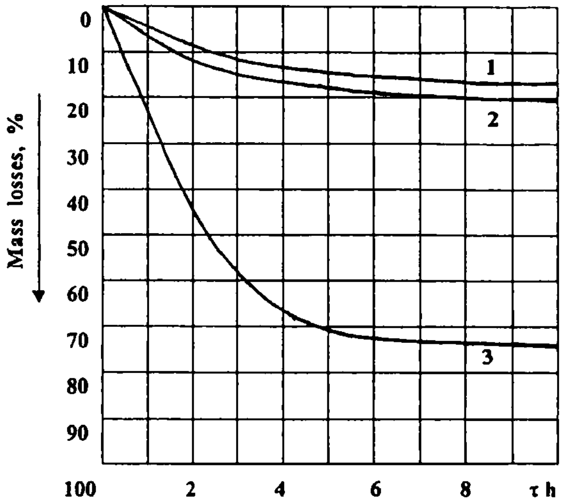


FIGURE 18 Thermogravimetric curves in isothermal conditions. Where curve 1 corresponds to oligomer XI, curve 2-X and curve 3-XIV.

Downloaded At: 10:29 19 January 2011

References

[1] Plueddemann, E. P. and Fanger, G. (1959). *J. Amer. Chem. Soc.*, **81**, 2632.
[2] Greber, G. and Metzinger, L. (1960). *Makrom. Chem.*, **39**, 189.
[3] Riffle, J. S., Yilgor, I., Tran, C., Wilkes, G. L., McGrath, J. E. and Bantia, A. K. (1983). "Epoxy Resin Chemistry II", *ACS Symp. Ser.*, **221**, 21.
[4] Gagnebien, D., Madec, P. J. and Marechal, E. (1985). *Eur. Polym. J.*, **21**, 289.
[5] Girgvliani, D. A., Khananashvili, L. M., Davitian, S. P., Khachatrian, A. R., Tsomaia, N. G. and Tonoyan, A. O. (1994). *J. Polym. Materials*, **25**, 65.
[6] Khananashvili, L. M., Bochorishvili, I. Z., Markarashvili, E. G. and Tsomaia, N. I. (1995). *Proceedings of the Academy of Sci. of Georgia*, Chem. Series, **20–21**, 35.
[7] Khananashvili, L. M., Tsomaia, N. I., Murachashvili, D. U., Girgvliani, D. A., Karchkhadze, M. G. and Sh, R. (1997). *J. Polym. Materials*, **37**, 65.
[8] Rao, B. S., Madec, P. J. and Marechal, E. (1986). *Makromol. Chem.*, Rapid Commun., 7, 703.
[9] Murachashvili, D. U., Khananashvili, L. M., Kopilov, V. M., Tsomaia, N. I. and Shkolnik, M. I. (1993). *Proceedings of the Academy of Sci. of Georgia*, Chem. Series, **19**, 201.
[10] Khananashvili, L., Gurgenidze, G., Karchkhadze, M. and Mukbaniani, O. (1998). *XVI D. Mendeleev Symposium in General and Applied Chemistry*, Sankt-Peterburg, p. 319.
[11] Mukbaniani, O. V., Khananashvili, L. M., Esartia, I. G. and Khaduri, S. (1994). *Intern. Journal of Polym. Mater.*, **22**(1–4), 131–139.
[12] Murachashvili, D., Khananashvili, L., Tsomaia, N., Kopilov, V., Shkolnik, M. and Khubulava, E. (1996). *Proceedings of the Academy of Sci. of Georgia*, Chem. Series, **22**, 36.

Downloaded At: 10:29 19 January 2011