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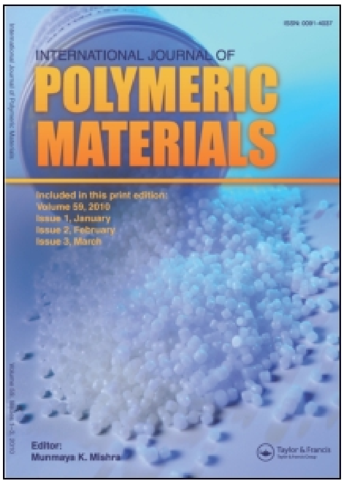

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Hydride Addition of Methylhydridesiloxanes to Dicyclopentadiene

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The reaction of hydride polyaddition of methylhydridesiloxanes to unsaturated carbocyclic compound–dicyclopentadiene, at the ratio of initial compounds 1 : 53 and 1 : 30, in the presence of platinum chlorohydric acid has been investigated. The hydride polyaddition reaction order, activation energies and rate constants were found. The polyorganosiloxanes with tricyclodecenyl fragment in the side chain, completely dissoluble in organic solvents were synthesized. The synthesized oligomers were characterized by ^1H and ^{13}C NMR, IR, thermogravimetric, gel permeation chromatographic, differential scanning calorimetric and X-ray methods.

Keywords: Organosiloxanes; Hydride polyaddition; Oligomers thermal-oxidative stability

INTRODUCTION

The properties of organosilicon polymers depend on the structure of a macromolecular chain and on the nature of the organic groups surrounding the silicon atom [1].

Therefore it is evident that effective methods of synthesis of new types of organosilicon co-polymers with complex and valuable

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*Corresponding author.

properties command a great importance. Particularly the synthesis of polyorganosiloxanes with unsaturated surrounding groups at the silicon atom, for obtaining siliconorganic rubbers [2] and for modifying carbochain polymers [3] is very interesting.

From this point of view the chemical modification reactions are very interesting. In literature the modification reactions of the linear polymethylvinylsiloxanes with tricyclodecenyl groups is known [4]. In this case the synthesized polymers are characterized with higher reactionability for vulcanization and thermal-oxydative stability. By the catalytic dehydrocondensation of polymethylhydridesiloxanes with hydroxyorganocyclosiloxanes in the presence of catalysts the polyorganosiloxanes with cyclic fragments in the side chain were synthesised [5]. By hydrosilylation reactions of methyl(ethyl)hydridesiloxanes with vinylorganocyclosiloxanes in the presence of platinum chlorohydric acid polyorganosiloxanes with carboorganocyclosiloxane fragments in the side chain were synthesized [6]. In both cases the insertion of reactionable cyclic fragments in the side chain leads to the rise of the thermal-oxydative stability and glass transition temperature of copolymers.

EXPERIMENTAL PART

The purity of initial dicyclopentadiene was controlled by its boiling temperature and refraction indexes. The organic solvents were cleaned 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.

The IR spectra of all the samples were taken on an UR-20 instrument, while the ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-250 spectrometer at 250 MHz in the solution of deuterium solvents as solvent and internal standard.

The starting materials for the synthesis of the linear siloxanes with tricyclodecenyl fragments in the side chain were α,ω-bis(trimethylsiloxy)methylhydridesiloxanes with various degrees of polymerization ($n \approx 30, 53$) and dicyclopentadiene.

Gel permeation chromatography (GPC) measurements were carried out by using toluene or THF as an eluent and RI detector. Standard polystyrenes or polydimethylsiloxanes were used for calibration. Gel permeation chromatography was carried out with the use of 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.

A Perkin-Elmer DSC-7 (differential scanning calorimeter) with a cooling accessory was used to determine the thermal transitions in oligomers. A heating and cooling scanning rate of 10°C/min was used. Glass transition temperatures (T_g) were read from the endothermic DSC traces, approximated to be midpoints between the extrapolated tangents to the baselines above and below the glass transition region.

Diffractograms were taken on a "Dron-2" instrument, using-Cu_α radiation without a filter, the angular velocity of the motor $\omega = 2$ deg/min.

The thermogravimetric investigations were carried out on a "Paulic-Paulic-Erdey" derivatograph model MOM-102. The test conditions were: temperature rise rate $\nu = 5$ deg/min, in the open area.

Hydride Addition of Methylhydridesiloxanes to Dicyclopentadiene (DCP)

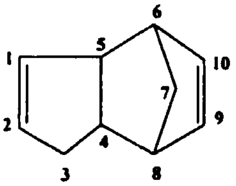
The hydrosilylation was carried out in the three-necked flask equipped with stirrer and reflux condenser with calcium chloride tube. The initial reagents: α,ω-bis(trimethylsilyl)methylhydridesiloxane and dicyclopentadiene were placed in the flask and thermostated in an oil bath until constant temperature was achieved. As a catalyst 0, 1 M solution of platinum chlorohydric acid in tetrahydrofuran ($5 \div 10 \times 10^{-5}$ g per 1 g of the starting substance) was used. The reaction was performed in argon atmosphere in the presence of toluene at temperature region of $60 \div 90$°C. Then the reaction mixture was connected to the vacuum line ($P = 1 \div 2$ mmHg) and the toluene and unreacted DCP was removed at a temperature range of 40 – 50°C.

RESULTS AND DISCUSSION

In the literature there is some information of obtaining tricyclodecenyl containing alkylsiloxanes by hydrosilylation of DCP by hydride-organochlorosilanes in the presence of platinum chlorohydric acid [7], in the presence cobalt and rhodium carbonyls [8]. It is known dimethylsiloxane copolymers with tricyclodecenyl groups in the chain [9]. These copolymers with unsaturated fragments in the chain are very interesting systems from a practical stand point, because they contain unsaturated bonds, which give the possibility to change the properties of organosilicon elastomers over a wide range.

For the purpose of synthesis of the linear organosilicon elastomers with tricyclodecenyl fragments in the side chain, the modification reactions of α,ω-bis(trimethylsiloxy)methylhydridesiloxanes ($n \approx 30$, 53) with DCP were studied. The hydrosilylation reactions were studied at 1 : 53 and 1 : 30 molecular ratio of initial compounds in the presence of platinum chlorohydric acid as catalyst. Preliminary heating of initial compounds in the temperature range of $60 \div 90°C$ in the presence of catalyst, showed that in these conditions no changes of initial compounds take place. Besides, there are no changes in the NMR and IR spectra of DCP and methylhydridesiloxanes. By gas–liquid chromatography it was established that the polymerization of DCP in this condition does not proceed.

As seen from the structure of DCP:



it contains two unsaturated bonds in "1–2" and "9–10" position. From literature data during hydrosilylation of DCP in case of a large amount of electron accepting groups containing organochlorosilanes (methyldichlorosilane) hydride addition at double bond proceeds at the "9–10" position. At a small amount of electron accepting groups (in case of dimethylchlorosilanes) the addition proceeds at both the "1–2" and "9–10" position. In the presence of electrodonor groups (in case of trimethylsilane) the hydrosilylation mainly proceeds at the

"1 - 2" position. It was possible that in our case the reaction have proceeded at the "1 - 2" position. As is known from the literature the electrophilic addition of H—Si≡ bond to DCP must proceed with the formation of transitional complex. The stability of the complex at "9 - 10" position because of steric difficulty is lower than the stability of the complex at "1 - 2" position. Because of that the addition occurs mainly at the "9 - 10" position.

In the ^1H NMR spectra of DCP, Figure 1, one can observe the multiplet resonance signals for unsaturated bonds centered at δ = 5,55 ppm and δ = 6,0 ppm. One can observe the protons in methylene groups at 7a and 7b positions centered at δ = 1,55 ppm and δ = 1,35 ppm (J_{hemin} = 14 Hz) $\delta H(3_{a,e})$ = 2,20 ppm.

In the ^1H NMR spectra of hydrosilylation product II, (Fig. 2), one can observe the unimportant resonance signals for protons in unsaturated fragment at "9 - 10" position, and mainly unchanged multiplet resonance signals at $\delta = 5{,}3 \div 5{,}7$ ppm, with integral intensity $\sim 1:10$. So, from ^1H NMR spectra of hydrosilylation product it is evident that the hydride addition mainly proceeds at "9 - 10" position and about 10% in "1 - 2" position. (See Tab. I).

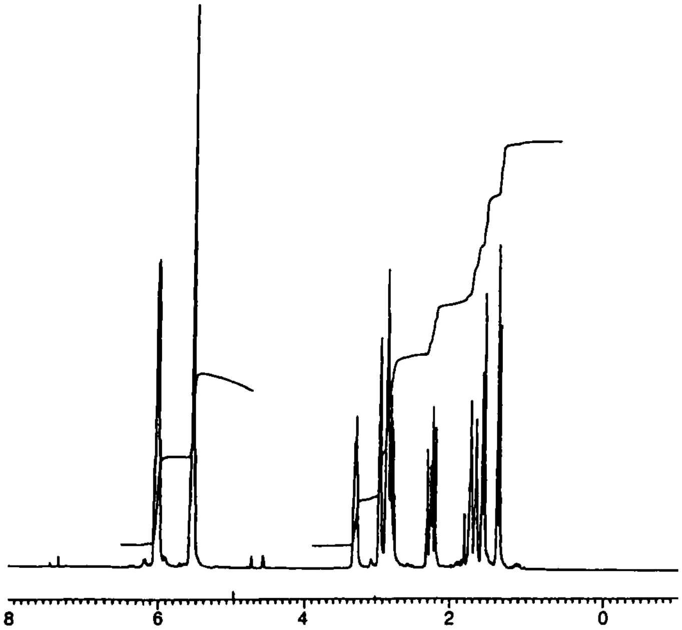


FIGURE 1 ^1H NMR spectra of dicyclopentadiene.

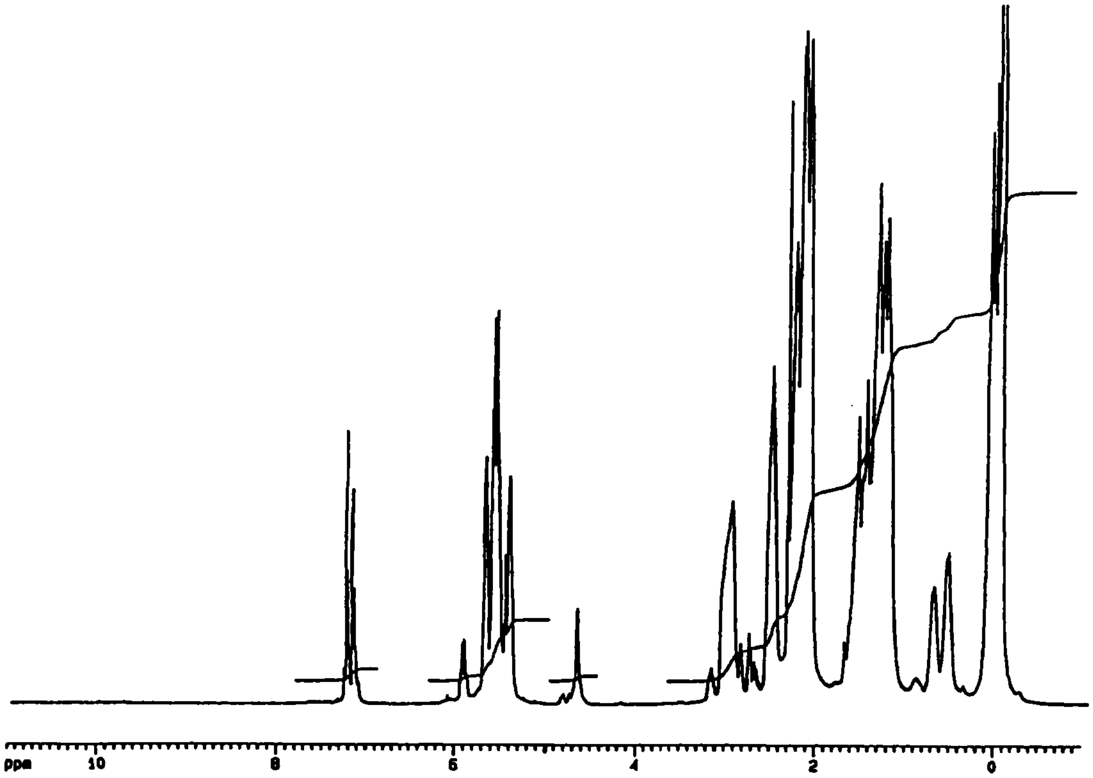
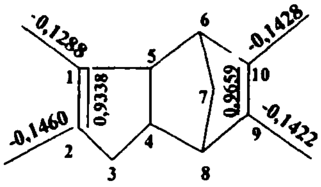


FIGURE 2 ^{1}H NMR spectra of α,ω-bis(trimethylsiloxy)methyltricyclodecenylsiloxane II.

TABLE I ^{1}H NMR spectra of dicyclopentadiene and methyltricyclodecenylsiloxane (II)

C—H bond	*H*-1	*H*-2	*H*-3	*H*-4	*H*-5	*H*-6	*H*-7	*H*-8	*H*-9	*H*-10
DCP (ppm)	5,95	5,95	2,20	1,67	1,67	2,22	1,40	2,17	5,50	5,50
II (ppm)	5,95	5,95	2,20	1,70	1,70	1,80	1,30	1,80	-	-

The above-mentioned conclusion conforms with quantum-chemical calculation. By quantum-chemical half emphiric method MNDO the electronic charges on the atoms and bond orders were calculated. The obtained results are presented on the diagram:



As seen from diagram, the higher value of the charge observed on the carbon atoms in "1 – 2" and "9 – 10" position. Which indicates that these carbon atoms are reactionable centers for electrophilic addition. Also, bond orders in "1 – 2" and "9 – 10" position are characterized with higher values. For example $P_{1,2}(\pi) = 0{,}9338$ and $P_{9,10}(\pi) = 0{,}9659$ (where index π showed bond orders of π components). Because $P_{9,10}(\pi) > P_{1,2}(\pi)$ it's possible to predict, that the addition is more likely with participation of $P_{9,10}\pi$ electrons. This conclusion does not except the addition in "1 – 2" position.

The hydrosilylation reaction was studied in the temperature range 60 ÷ 90°C. It was established that during the reaction in melt condition, at the initial stages of addition, three dimensional systems were obtained, which may be explained by intermolecular reactions inmacro chain. For the purpose of synthesis of soluble organosiloxanes the reactions were carried out in anhydrous toluene solution ($C = 0{,}1017$ mole/l). The course of the reaction was observed by the decrease of the amount of active Si—H groups. As seen from Figure 3, with the rise of temperature the amount of hydrosilylation reaction increases. At 60°C temperature the conversion of active Si—H bonds after 5 h hydrosilylation is about 61% (Fig. 3, curve 1), with the rise of the temperature the conversion of active Si—H bonds increases and at 90°C temperature it consists about 85% (curve 4).

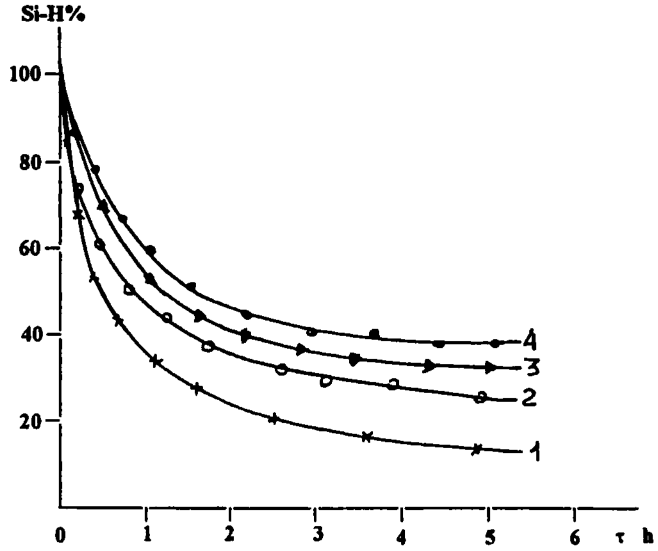
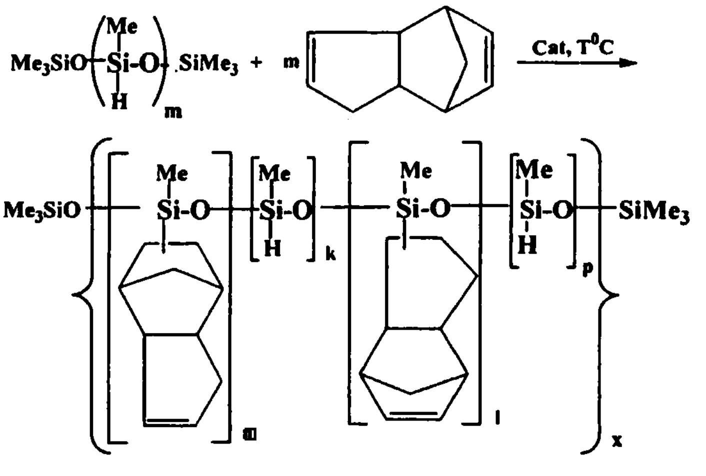


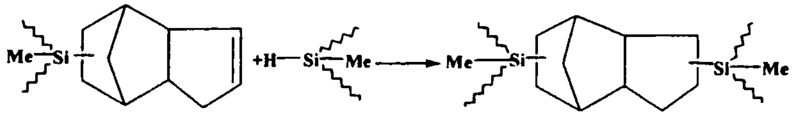
FIGURE 3 Dependence of changes of active Si—H% groups on the time upon of hydride addition of α,ω-bis(trimethylsiloxy)methylhydridesiloxanes to dicyclopentadiene, where curve 1 is at 90°C, curve 2 is at 80°C, curve 3 is at 70°C and curve 4 is at 60°C.

The hydrosilylation proceeds vigorously at the first 90–100 min, after that the conversion of active Si—H bonds slows. On the basis of experimental investigations it is possible to assume that hydrosilylation mainly proceeds according to the following scheme:



where: $(n+k+l+p)x = m$; $m \approx 30$, $t = 90°C(I)$; $m \approx 53$, $t = 60°C(II)$; $70°C(II^1)$, $80°C(II^2)$, $90°C(II^3)$.

It was established that with the rise of temperature three dimensional polymers are obtained. During hydrosilylation at 90°C about 20% insoluble polymers were obtained, this may be explained by the secondary interchain reactions on the basis of catalyst in the reaction system:



Consequently in DCP, the —CH=CH— bond in "1-2" position, as the unsaturated bond in "9-10" position, is characterized with higher reactability preference to hydrosilylation. The synthesized oligomers are transparent products well soluble in ordinary organic solvents, with $\eta = 0{,}07 \div 0{,}11$. Some physical-chemical properties of the oligomers are presented in Table II.

In the IR spectra of synthesized oligomers one can observe absorption bands characteristic for —CH=CH— bonds at 1600 and 3550 cm^{-1}, the absorption bands at 2165, 1275 and 1020 cm^{-1}, characteristic for Si—H, Si—Me and SiOSi bonds respectively.

In Figure 4 the dependence of reverse concentration of the reactant on the time is presented. One can see that at the initial stages the hydrosilylation reaction is of second order. The hydrosilylation reaction rate constants at various temperatures were

TABLE II Physical-chemical properties of methyltricyclodecenylhydridesiloxanes

Oligomer, S	*Yield, %*	$\eta^* \cdot {}_{SP}$	T_g, °C	$\bar{M}_w \times 10^3$	*P, polydisp.*	*5%, mass losses*	d_1, Å
I	85	0,08	−1	7,8	2,6	240	9,10
I^1	65	0,12	+8	82,1	21,8	300	9,33
II	67	0,07	–	–	–	–	–
II^1	70	0,08	+2	7,8	1,8	–	–
II^2	75	0,09	–	–	–	–	–
II^3	83	0,09	+6	10,3	2,3	270	9,33

* In 1% solution of toluene at 25°C.

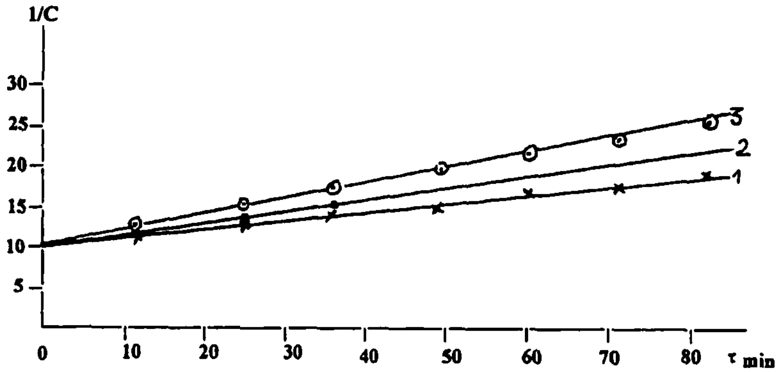


FIGURE 4 Dependence of reverse concentration on the time, where curve 1 is at 60°C, curve 2 is at 70°C and curve 3 is at 80°C.

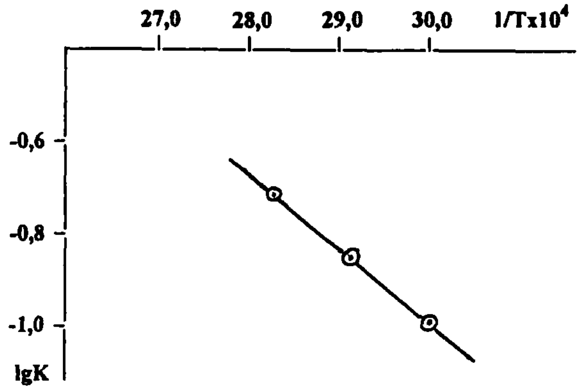


FIGURE 5 Dependence of reverse temperature on the logarithm of the rate constants of hydride addition.

calculated: $K_{60}°C = 1{,}051 \times 10^{-1}$, $K_{70}°C = 1{,}405 \times 10^{-1}$, $K_{80}°C = 1{,}944 \times 10^{-1}$. The temperature coefficient of hydrosilylation reaction was determined to be $\gamma \approx 1{,}34$.

Figure 5 shows the dependence of the logarithms of the hydrosilylation reaction rate constants on the reverse temperature. From these data the activation energy of hydrosilylation reaction was calculated to be equal to $E = 32{,}3$ KJ/mole.

The synthesized oligomers were studied by GPC method. Figure 6 shows the molecular weight distribution of oligomer I. $M_w \approx 7{,}8 \times 10^3$ and polydispersity is equal to $p \approx 2{,}6$. Whence it follows, that in case of full hydrosilylation $\bar{M}_w$ does not exceed 6×10^3. Increased molecular weight once again proved that the reaction proceeds through macromolecular interchain hydride addition. The oligomer I (30% toluene solution) was further heated for several hours at 80–90°C temperature interval, at this time the value of active Si—H groups decreased from 18% down to 3%. After filtration the toluene was removed at 40–50°C in vacuum ($P = 1 \div 2$ mmHg) up to constant mass, and transparent yellow oligomer I^1 was obtained which is soluble in ordinary organic solvents. GPC analysis, Figure 7, showed that during the additional heating the macromolecular interchain hydride addition took place and polydisperse oligomer I^1 with $\bar{M}_{w'} \approx 8{,}3 \times 10^4$ and $p \approx 21{,}8$ was obtained.

The TGA analysis of methyltricyclodecenylsiloxane II^2 was carried out. As seen from Figure 8, thermal-oxidative stability of tricyclodecenyl containing methylsiloxanes is higher than the thermal-oxidative stability of the initial methylhydridesiloxane. The main destruction process proceeds at ~50–60°C higher than for the methylhydridesiloxanes.

By DSC analysis (Fig. 9) it was shown that the first phase transition for oligomer I, which corresponds to glass transition temperature (T_g) is observed at ~ –1°C and for oligomer I^1 it is observed at ~ +8°C. With an increase of amount of tricyclodecenyl fragments in the linear siloxane chain (with an increase of the amount of hydride addition) the T_g of oligomers rises (see Fig. 9, curves 1–4).

The tricyclodecenyl containing methylhydridesiloxane oligomers are amorphous, single phase systems. With an increase of the amount of tricyclodecenyl fragments in dimethylsiloxane chain the value of the interchain distances d_1 slightly increases.

The synthesized tricyclodecenyl and hydride containing linear methylsiloxanes are interesting products, because they contain reactionable functional groups which easily enter into interchain addition reactions. This gives us the possibility to use such oligomers to prepare organosilicon rubbers.

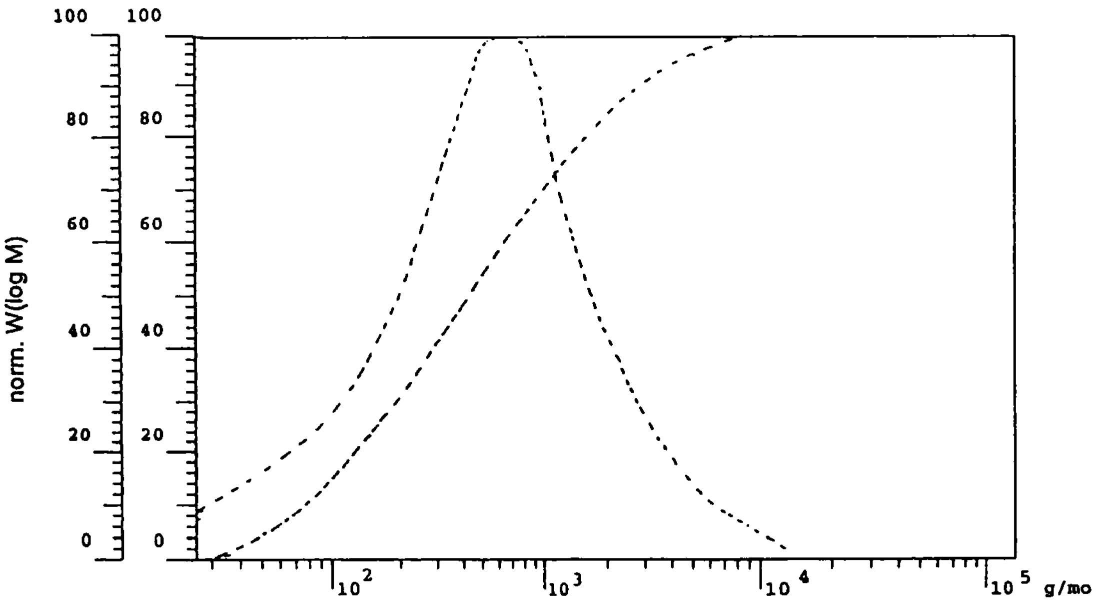


FIGURE 6 Gel permeation chromatographic curves of oligomer I.

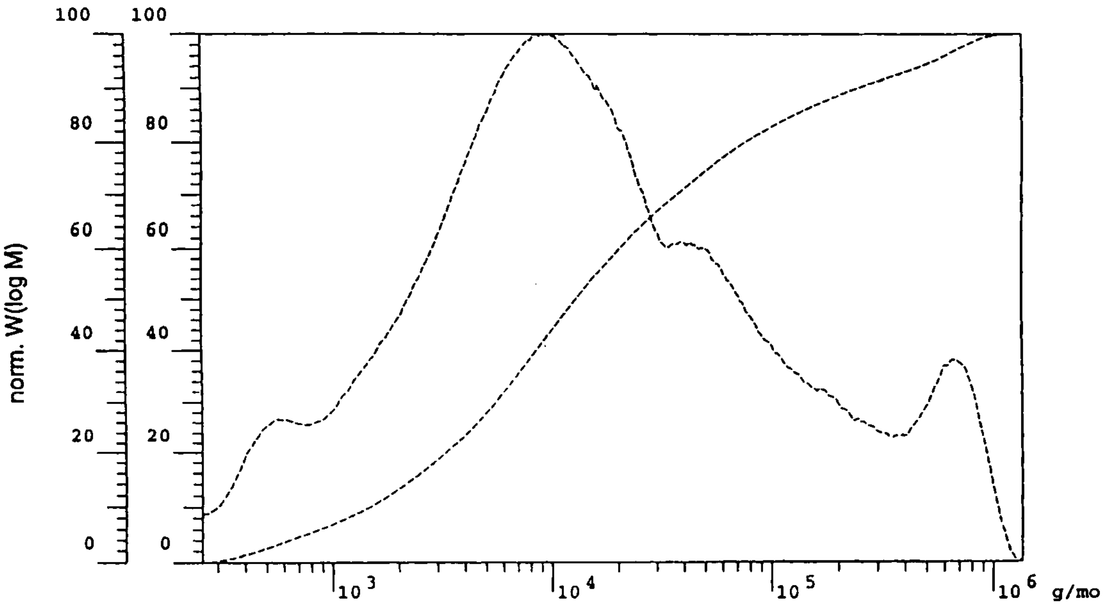


FIGURE 7 Gel permeation chromatographic curves of oligomer I[1].

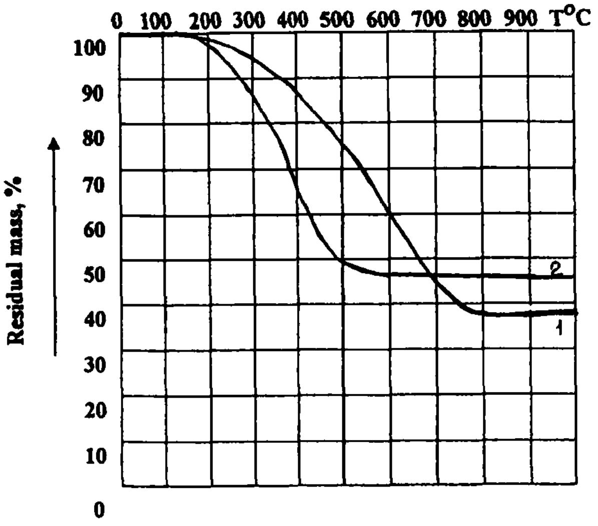


FIGURE 8 Thermogravimetric curves of oligomers, where curve 1 is for oligomer II^2 and curve 2 is for initial methylhydridesiloxane oligomer ($n \approx 53$).

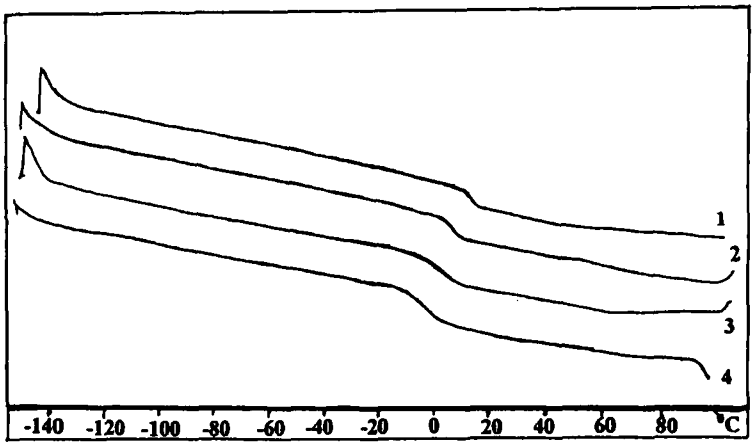


FIGURE 9 DSC curves of oligomers, where curve 1 is for oligomer I^1, curve 2 is for oligomer II^3, curve 1 is for oligomer II^1, curve 1 is for oligomer I.

References

[1] Mukbaniani, O. V. and Khananashvili, L. M. (1994). *Intern. J. Polymer. Materials*, 27, 31.

[2] Aneli, G. N., Koberidze, Kh. E., Mukbaniani, O. V., Karchkhadze, M. G. and Khananashvili, L. M. (1998). *Russian Polymer News*, 3(4), 7.

[3] Galashina, N. M. (1994). *Vysokomol. Soed.*, **36**A(4), 640.
[4] Aneli, G. N., Mukbaniani, O. V., Karchkhadze, M. G., Koberidze, Kh. E., Tkeshelashvili, R. Sh. and Khananashvili, L. M., *Georgian Patent*, N1348101–96.
[5] Mukbaniani, O. V., Khananashvili, L. M., Esartia, I. G. and Khaduri, S. D. (1994). *Intern. J. Polymer. Materials*, **24**, 211.
[6] Mukbaniani, O. V. and Khananashvili, L. M. (1994). *Intern. J. Polymer. Materials*, **27**, 31.
[7] Petrov, A. D., Plate, A. F., Chernishev, E. A., Dolgaia, M. E., Belikova, N. A., Krasnova, T. L., Leitis, L. A., Priashnikova, M. A., Taits, G. S. and Kozirkin, B. I. (1961). *Zhurn. Obshch. Khimii*, **31**, 1199.
[8] Magomedov, G. K. I., Shkolnik, O. V., Khananashvili, L. M., Nakaidze, L. I. and Katsitadze, M. G. (1988). *Zhurn. Obshch. Khimii*, **59**, 104.
[9] Nogaideli, A. I., Khananashvili, L. M., Nakaidze, L. I., Chogovadze, T. V., Tskhovrebashvili, V. S., Volkova, R. V. and Nogaideli, G. A. (1978). *Dokl. Akad. Nauk GSSR*, **92**, 341.