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Modification Reactions of Methylhydrosiloxanes with Tricyclodecadiene

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Summary: The reaction of hydride polyaddition of methylhydridesiloxane and methylhydridesiloxane-dimethylsiloxane oligomers to unsaturated carbocyclic compound - tricyclodecadiene, at the various ratio of initial compounds, in the presence of platinum hydrochloric acid has been investigated. It was shown that hydrosilylation reaction proceeds both to 1.2 and 9.10 positions and by intermolecular with formation of branching systems. The polyorganosiloxanes with tricyclodecenyl fragment in the side chain, completely soluble in organic solvents were synthesized. For fully characterization of hydride addition of methylhydridesiloxane to tricyclodecadiene, by quantum-chemical half empiric AM1 method, for all initial, intermediate and final products, in modelling reaction of hydrosilylation of methyldimethoxysilane to tricyclodecadiene, the heats of formations (ΔH_f), change of energy (ΔH) of the system depending on the change of distance ($R_{C\text{-}Si}$) between $\equiv$C-Si$\equiv$ bonds, also the charges values (q) on the atoms, dipole moments (μ) and bonds orders (Pij) are calculated. It was concluded, that the course of hydride addition of modelling reaction of methyldimethoxysilane to tricyclodecadiene energetically is more favourable by 9.10-addition. The hydride polyaddition reaction order, activation energies and rate constants were found. The synthesized oligomers were characterized by ^{1}H and ^{13}C NMR, FTIR, thermogravimetry, gel permeation chromatography, differential scanning calorimetry and wide angle X-ray methods.

Keywords: hydride polyaddition; oligomers; organosiloxanes; thermal-oxidative stability

Introduction

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

Therefore it's evident that effective methods of synthesis of new type siliconorganic co-polymers with complex's valuable properties attach a great importance. Particularly the synthesis of polyorg-anosiloxanes with un-saturating surrounding groups at silicon atom, for receiving of siliconorganic rubbers[2] and for modification carbo chain polymers[3] is very interesting.

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] From this point of view the chemical modification reactions of poly(methylhydro)siloxanes are very interesting. In lit-

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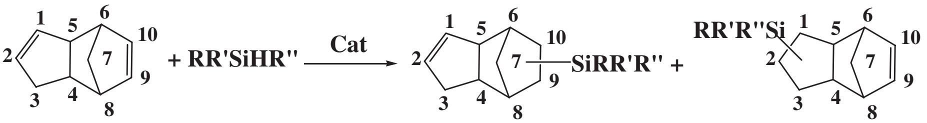
erature the modification reactions of the linear polymethylvinylsiloxanes with cyclopentadiene groups is known.[7] In this case the synhesized polymers are characterized with higher reaction ability for vulcanization and thermal-oxidative stability.

From literature[8] it's known, that electrophilic addition of monomer type methylhydrochlorosilanes to tricyclodecadiene in the presence of Spier catalyst proceeds both to 9.10 and 1.2 addition depending on the nature and amount of organic groups at silicone atoms, according to the following Scheme:



Where: $R = R' = R'' = $ Alk, Ar; $R \neq R' \neq R'' \neq$ Alk, Ar; $R'' = $ CI.

By the authors[9] it was shown that using in this reactions such catalysts as $Rh_4(CO)_{12}$ or $Co_2(CO)_8$ the hydrosilylation proceeds selective mainly via 9,10-addition, without obtaining isomeric adducts.

Experimental Part

Materials and Techniques

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

The initial α,ω–bis(trimethylsiloxy) methylhydridesiloxane with degree of polymerization ~m ≈ 30, 53 and α,ω–bis (trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane oligomer with degree of polymerization ~m ≈ 33, n ≈ 23 tricyclodecadiene and catalyst H_2PtCl_6 were obtained from Sigma-Aldrich and used as received. The organic solvents were cleaned by drying and distillation.

The organic solvents were cleaned by drying and distillation. The purity of initial tricyclodecadiene was controlled by its boiling temperature and refraction indexes. The purity of the starting compounds was controlled by gas-liquid chromatography "LKhM-8 MD", (Russian model) phase SKTF-100 (10%), the NAW chromosorb, carrier gas He, the 2M column.

FTIR spectra were obtained on Nicolet Nexus 470 with MCTB detector. ^{1}H and ^{13}C spectra were recorded on AC-250 spectrometer at 250 MHz in the solution of deuterium solvents as solvent and internal standard.

Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 the thermogravimetric analyser at ~10°C/min. Differential scanning calorimetric analysis was performed on a Perkin-Elmer DSC-7. Heating and cooling scanning rates were ~5C/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 Ultrastyragel columns (Waters, USA). Sample concentration was approximately 3% by weight in toluene; a typical injection volume for the siloxane was 5 μL. 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$_($ radiation. The values were measured without a filter, and the angular velocity of the motor was ~2 deg/min.

Hydride Addition of Methylhydrosiloxane to Tricyclodecadiene (TCD)

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)methylhydrosiloxane and tricyclodecadiene 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 hydrochloric acid in tetrahydrofuran ($5 \div 10 \times 10^{-5}$ g per 1 g of the starting substance) was used. The reaction was performed in the argon atmosphere in the presence of toluene at temperature region $60 \div 90\,^{\circ}$C. Then the reaction mixture was connected to the vacuum ($P = 1 \div 2$ mmHg) and the toluene and unreacted TCD was removed in the temperature range 40–50 °C under the vacuum.

Results and Discussion

In literature there is some information of receiving tricyclodecenyl containing alkyl siloxanes by hydrosilylation of TCD by hydrideorganochlorosilanes in the presence of platinum hydrochloric acid,[7] in the presence cobalt and rhodium carbonyls.[8] It's known the polycondensation type organo-inorganic copolymers with tricyclodecenyl groups in the chain.[9] These above mentioned copolymers with unsaturated fragments in the chain by practical standpoint are very interesting systems, because they contain unsaturated bonds, which give us possibility to change the properties of obtained siliconorganic elastomers in a wide range.

Preliminary heating of initial compounds in the temperature range of $60 \div 90\,^{\circ}$C in the presence of catalyst, showed that in these conditions polymerization of tricyclodecadiene, break in siloxane backbone, or elimination of methane do not take place. Besides, there are no changes in the NMR and FTIR spectra of TCD and methylhydrosiloxanes. By gas-liquid chromatography it was established that the polymerization of TCD in this condition does not proceed.

For the purpose of synthesis of the linear siliconorganic elastomers with tricyclodecenyl fragments in the side chain the modification reactions of α,ω-bis(trimethylsiloxy)methylhydrosiloxane ($n \approx 30,53$) and α, ω-bis(trimethylsiloxy)methylhydrosiloxane-dimethylsiloxane with TCD were studied. The hydrosilylation reactions were studied at 1:30, 1:53 and 1:25 molecular ratio of initial compounds in the presence of platinum hydrochloric acid as a catalyst. As it's seen from the molecular structure of TCD it contains two unsaturated bonds in 1.2 and 9.10 position. From literature data[8,9] during hydrosilylation of TCD in case of a big amount of electro acceptoric groups containing organochlorosilanes (methyldichlorosilane) hydride addition at double bond proceeds to 9.10 positions. At a small amount of electro acceptoric groups (in case of trimethylchlorosilane) the addition proceeds both to 1.2 and 9.10 position. In the presence of electro donor groups (in case of trimethylsilane) the hydrosilylation mainly proceeds to 1.2 positions. It was possible that in our case the reaction must be proceeding to 1.2 positions. As it's known from literature the electrophilic addition of $\equiv$Si-H bond to TCD must be 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 to 1.2 position, because of that the addition mainly must be proceeded to 9.10 position.

In the ^{1}H NMR spectra of hydrosilylation product II (Figure 1) one can observe the resonance unimportant 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 ~1:10. So, from ^{1}H NMR spectra of hydrosilylation product it's evident that the hydride addition mainly proceeds at 9.10 position and about 10% in 1.2 position.

The above-mentioned conclusion is in conformity with quantum-chemical calculation. By Quantum-chemical semi empiric method AM1 (Austin Model) the electronic characteristics: the charges on the atoms and bonds orders were calculated. The obtained results are presented on the Scheme 1.

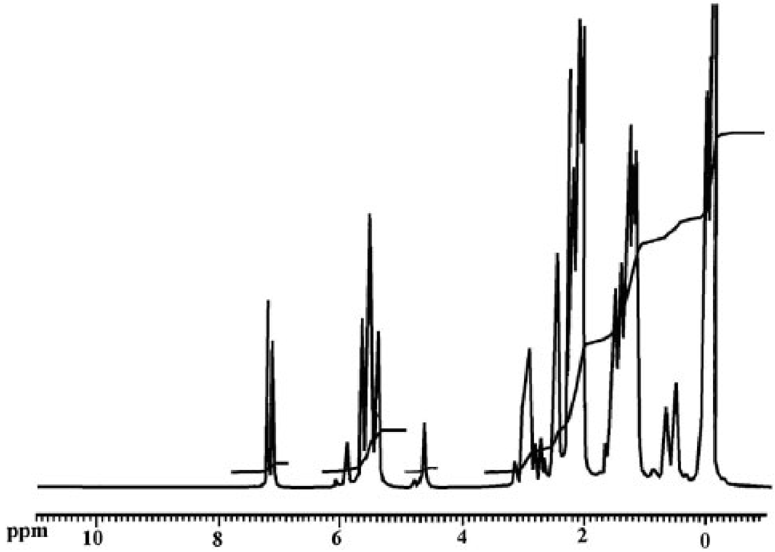
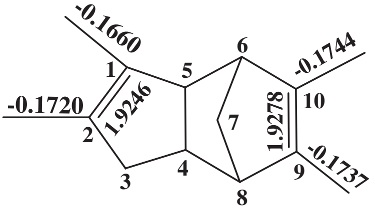


Figure 1.
^{1}H NMR spectrum of α,ω-bis(trimethylsiloxy)methyltricyclodecenylsiloxane II.

^{1}H NMR resonance signals of TCD, oligomers II and III are presented in Table 1.

As it's seen from Scheme 1, the higher value of the charge observed on the carbon atoms in 1.2 and 9.10 position. This indicates that these carbon atoms are reactionable centres for electrophilic addition. Also, bond orders in 1.2 and 9.10 position are characterized with higher values. For example $P_{1.2}(\pi) = 1.9246$ and $P_{9.10}(\pi) = 1.9278$ (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 possible with participation of $P_{9.10}(\pi)$ electrons. This conclusion does not except the addition in 1.2 position.



Scheme 1.
The charges on the atoms and bond orders in TDC molecule.

The hydrosilylation reaction was studied at the constant temperature, in the range 60 ÷ 90 °C. It was established that during the reaction in melt condition, at beginning stages of addition, three dimensional systems were obtained, which may be explained by intermolecular reactions in macro chain. For the purpose of synthesis of soluble organosiloxanes the reaction were carried out in absolute toluene solution ($C = 0.1017$ mol/l). The course of the

Table 1.
^{1}H NMR resonance signals of TCD and oligomers (II, III).

C–H bond	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10
TCD (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	—	—
III (ppm)	5.96	5,96	2,20	1,70	1,70	1,80	1,30	1,80	—	—

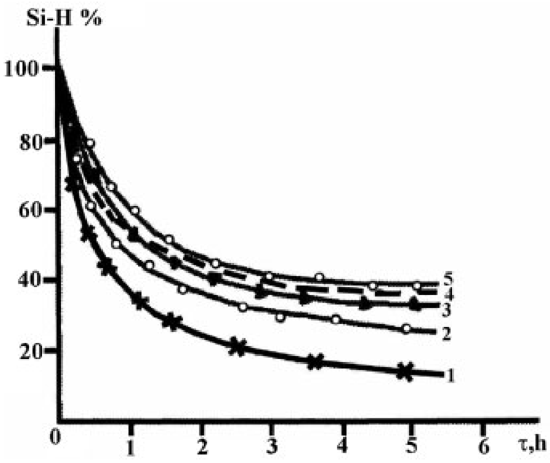
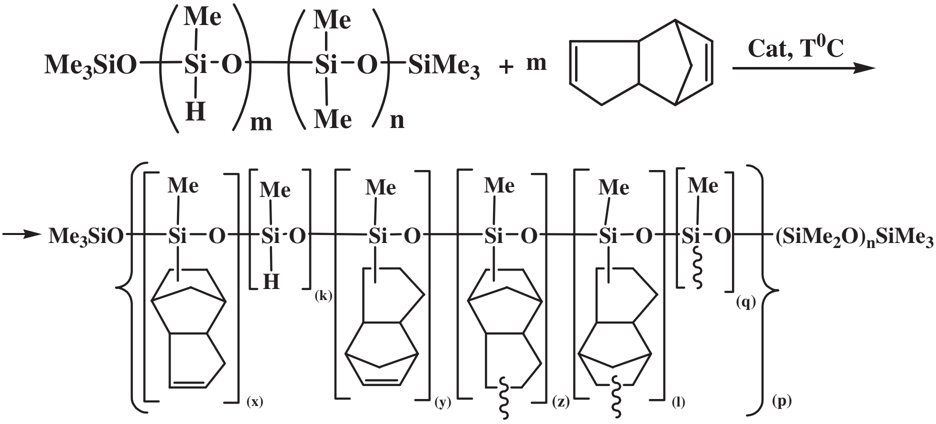


Figure 2.
Dependence of changes of active Si-H% groups on the time upon of hydride addition of α,ω-bis(trimethylsiloxy)methylhydrosiloxane to tricyclodecadiene, where curve 1 is at 90 °C, curve 3 is at 80 °C, curve 4 is at 70 °C and curve 5 is at 60 °C. Curve 2 corresponds to hydride addition of α,ω-bis(trimethylsiloxy)methylhydrosiloxane-dimethyl siloxane to tricyclodecadiene at 90 °C.

reaction was observed by the decrease of the amount of active ≡Si-H groups (Figure 2).

It was shown that with the increase of temperature the depth of hydrosilylation increases. At 60 °C the conversion of active ≡Si-H groups after 5 h is about 61% (Figure 2, curve 4), at 90 °C the conversion is equal to 85% (Fig. 2, curve 1). In case of methylhydrosiloxane-dimethylsiloxane oligomer the conversion of active ≡Si-H groups at 90 °C is ~75%.

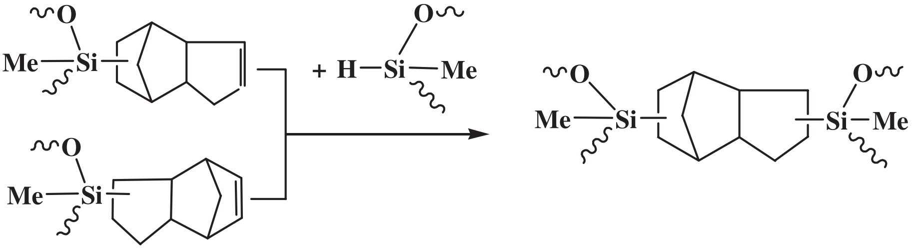
The hydrosilylation proceeds vigorously at first 90–100 min, after that the conversion of active ≡Si-H bonds increases slightly. On the bases of experimental investigations it's possible to assume that hydrosilylation mainly proceeds with obtaining of various linked branching systems, according to the following Scheme 2:



Scheme 2.
Hydrosilylation reaction of α,ω-bis(trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane oligomer to tricyclodecadiene.

Where: $[(x)+(k)+(y)+(z)+(l)+(q)](p) = m \approx 30, n = 0$: 90 °C(I) $m \approx 53$, 60 °C(II^1); 70 °C(II^2), 80 °C(II^3), 90 °C (II); $[(x)+(k)+(y)+(z)+(l)+(q)](p) = m \approx 30$, $m \approx 33$, $n = 23$: 90 °C (III).

It was established that with the rise of temperature cross-linked polymers are obtained. During hydrosilylation at 90 °C at 85% conversion of active ≡Si-H bonds about 33–35% insoluble polymers were obtained, this may be explained by the secondary interchain hydrosilylation reactions on the bases of catalyst in reaction system, according to the Scheme 3:



Scheme 3.
Possible scheme of inter-molecular hydrosilylation reaction.

Consequently in TCD, –CH=CH– bond in 1.2 position as unsaturated bond in 9.10 position is characterized with higher reaction ability reference to hydrosilylation. Therefore for reception of soluble copolymers hydrosilylation reaction stopped up to achievement 75–80% of conversion of active ≡Si-H groups. Then the reaction mixture was connected to the vacuum ($P = 1 \div 2$ mmHg) and the toluene and un-reacted TCD was removed in the temperature range 40–50 °C under the vacuum up to constant weight. The synthesized copolymers are transparent, opalescent viscous products well soluble in ordinary organic solvents with $\eta = 0.07 \div 0.13$. Some physical-chemical properties of oligomers are presented in Table 2.

In the FTIR 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 ≡Si-O-Si≡ linear bonds accordingly.

For fully characterization of hydride addition of methylhydridesiloxane to tricyclodecadiene, by quantum-chemical semi empiric AM1 method,[9] for all initial, intermediate and final products, in modelling reaction of hydrosilylation of methyldimethoxysilane to tricyclodecadiene, the heats of formations (ΔH_f), change of energy (ΔH) of the system depending on the change of distance ($R_{C\text{-}Si}$) between ≡C-Si≡ bonds, also the charges values (q) on the

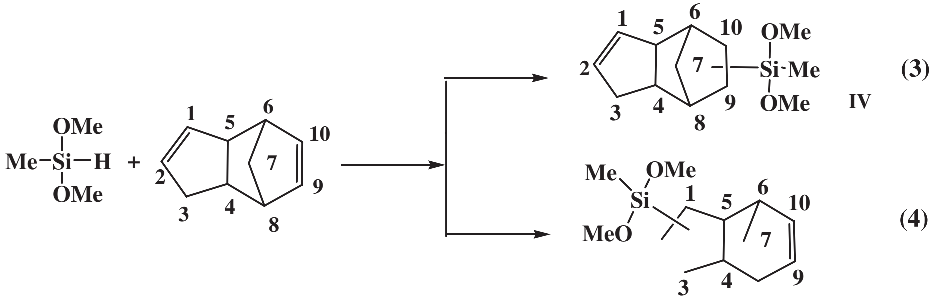
Table 2.
Physical-chemical properties of methyl(tricyclodecenyl)(hydride)siloxanes.

No	Yield, %	React. Temp-re °C	η^*_{sp}	T_g, °C	$\overline{M}_\omega \times 10^{-3}$	P, Polydisp	5%, mass losses	d_1, Å
I	85	90	0.08	−1	7.8	2.6	240	9.10
I^1	65	—	0.13	+8	82.1	21.8	300	9.33
II^1	83	60	0.07	—	—	—	—	—
II^2	75	70	0.08	+2	7.8	1.8	—	—
II^3	70	80	0.09	—	—	—	—	—
II	67	90	0.09	+6	10.3	2.3	270	9.33
III	70	70	0.11	−15	—	—	250	8.63

* In 1% solution of toluene at 25 °C.

atoms, dipole moments (μ) and bonds or-ders (Pij) are calculated.

For the beginning the modelling reaction of hydride addition of [$Me(MeO)_2SiH$] methyldimethoxysilane to tricyclodecadiene to 9.10 and 1.2 direction was considered. The modelling reactions of 9.10 additions and 1.2 additions with formation of compound IV and V proceeds according to the following Schemes 4 and 5:



Scheme 4–5.
Modelling reaction of hydrosilylation of methyldimethoxysilane [$Me(MeO)_2SiH$] to tricyclodecadiene to 9.10 (3) and 1.2 direction (4).

The distances between the double bonded carbon atoms (C_{10}, C_9 and C_1, C_2) and silicon atoms in tricyclodecadiene was taken about 1.0 Å more than the bond length, expected in a product. The change step of distances between silicon atom and double bonded carbon atom was ~0.05 Å. Dependence of change of energy (ΔH) calculated by the AM1 method as a function of the distance ($R_{C\text{-}Si}$) between silicon and carbon atoms are presented on the Figure 3.

As it is seen from Figure 3, at approximation of silicon to atom of carbon (C_{10}) up to $R_{C_{10}-Si} = 2.26$ and $R_{C_1-Si} = 2.30$ Å distances the energy of system rises. at the same time the bond order between double bonded carbon atoms in a molecule of tricyclodecadiene decreases and in modelling compound the process of formation of

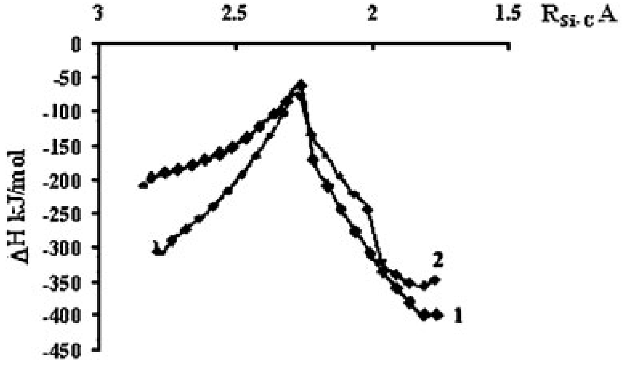


Figure 3.
Dependence of changes of energy (ΔH) on distances ($R_{C_{10}-Si}$) between silicon and carbon atoms during of modelling hydrosilylation reaction of methyldimethoxysilane to tricyclodecadiene. Where curve 1 corresponds to 9.10 addition and curve 2–1.2 additions.

new bonds ($R_{C_{10}-Si} = 0.015 - 0.105$ and $P_{C_9-H} = 0.0006 - 0.063$; $R_{C_1-Si} = 0.0085 - 0.853$ and $P_{C_9-H} = 0.0009 - 0.011$) is observed. In case of distance up to 2.21 Å and 2.25 Å the energy of system sharply decreases, the double C=C bond passes in ordinary C–C bond ($P_{C_{10}-C_9} = 0.991$ and $P_{C_1-C_2} = 0.980$).

With consecutive reduction of distances the system energy monotonously decreases and with strengthening formed new bonds. The heat of formation of the product IV and V ($\Delta H = -399.129$ kJ/mol) is in a good correlation with calculated heat of formation ($\Delta H = -399.012$ kJ/mol) of compounds IV and V obtained by hydride addition of methyldimethoxysilane to tricyclodecadiene at 9.10 or 1.2 direction. activation energy of 9.10 addition of modelling reaction is equal to $E_{act} = 133.21$ kJ/mol, while the activation energy of 1.2-addition of modelling reaction is equal to $E_{act} = 218.67$ kJ/mol.

Thus at comparison of the curves 1 and 2 (Figure 3), and also activation energy (the character of curve of change of energy and the value of bond orders) one can be concluded, that the course of modelling reaction of hydride addition of methyldimethoxysilane to tricyclodecadiene energetically is more favourable by 9.10 addition, that is in agreement with NMR spectral data.

From the dependence of reverse concentration of the reactant on the time is presented. One can see that at the beginning stages the hydrosilylation is the reaction of the second order. The hydrosilylation reaction rate constants at various temperatures were calculated: $k^{0}_{60C} = 1.051 \times 10^{-1}$, $k^{0}_{70C} = 1.405 \times 10^{-1}$, $k^{0}_{80C} = 1.944 \times \times 10^{-1}$ l/mol · s.

From the dependence of logarithm of the hydrosilylation reaction rate constants on the reverse temperature the activation energy of hydrosilylation reaction of methylhydridesiloxane to tricyclodecadiene was calculated $\sim E = 32.3$ kJ/mol.

The synthesized oligomers were studied by GPC method and it was shown that oligomer I had monomodal molecular weight distribution with $\sim \overline{M}_{\omega} \approx 7.8 \times 10^3$ and polydispersity is equal to $p \approx 2.6$. Whence it follows, that in case of full hydrosilylation $\overline{M}_{\omega}$ does not exceed 6×10^3. Increased molecular weight once again proved that the hydrosilylation reaction proceeds to macromolecular interchain hydride addition.

The oligomer I (30% toluene solution) was heated additionally for 4–5 hours at 80–90 °C temperature interval, at this time the value of active ≡Si-H group's decreases from 18% up 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 (65%) was received, which is soluble in ordinary organic solvents.

By GPC analysis it was shown that during additional heating the macromolecular intermolecular hydride addition takes place and oligomer I^1 with $\overline{M}_{\omega} \approx 8.3 \times 10^4$ and $p \approx 21.8$ were received.

The TGA analysis of methylsiloxane oligomers containing tricyclodecenyl fragments in the side chain was carried out and it was shown that they are characterized by higher thermal oxidative stability than trimethylsiloxy group blocked polydimethylsiloxanes. 5% mass loses for obtaining oligomers II^2 and III is observed in the range 290–300 °C. The main destruction process proceeds in 350–700 °C the temperature range, after 700 °C the mass losses did not observed. The oligomer III is characterized by lower thermal-oxidative stability, then oligomer II^2.

By DSC analysis it was shown that the first temperature transition for oligomer I, which corresponds to glass transition temperature (T_g) observed at ~ -1 °C and for oligomer I^1 at $\sim +8$ °C. With an increase of amount of tricyclodecenyl fragments in the linear siloxane chain (with an increase of the depth of hydride addition) the T_g of oligomers rises. For oligomer III glass transition temperature is equal to ~ -15 °C.

The tricyclodecenyl containing methylhydridesiloxane oligomers are amorphous one phase systems. With an increase of amount of tricyclodecenyl fragments in dimethylsiloxane chain the value of interchain distances d_1 slightly raises from 8.63 Å up to 9.33 Å.

Conclusion

So the reaction of hydride polyaddition of methylhydrosiloxane and methylhydrosiloxane-dimethylsiloxane oligomers to tricyclodecadiene, at the various ratios of initial compounds, in the presence of platinum hydrochloric acid has been investigated and thermo reactive methylsiloxane oligomers with tricyclodecenyl fragments at silicon have been obtained.

The synthesized tricyclodecenyl and hydride group containing methylsiloxane oligomers are interesting products, because they contain reactionable functional groups which easily enter in intermolecular hydrosilylation reaction at the expense of in system existence platinum hydrochloric acid that gives us possibility to use such oligomer to prepare siliconorganic rubbers and for modification of carbo chain elastomers.

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