Synthesis and Study of Organosilicon Hydroxymethylated Phenols

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Abstract—A series of (hydroxymethyl)hydroxyphenyldimethylsiloxanes of linear and branched structures were synthesized by the reaction with formaldehyde in aqueous alkaline medium of organosilicon phenols of general formula R'[Si(CH₃)₂O]_n[Si(CH₃)RO]_mSiMe₂R', where R' was 4-hydroxy-3-methoxyphenylpropyl, R was methyl or 4-hydroxy-3-methoxyphenylpropyl. The structure and composition of the siloxanes were confirmed by elemental analysis, NMR and IR spectroscopy. The homocondensation of (hydroxymethyl)hydroxyphenyl-dimethylsiloxanes at the hydroxymethyl groups was investigated. A possibility of reaction of (hydroxymethyl) hydroxyphenyldimethylsiloxanes with phenol-formaldehyde resin to form copolymers was demonstrated.

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The organosilicon compounds containing reactive phenol groups at the silicon atom are of interest as the starting monomers and oligomers for obtaining various silicon-containing polymers [1]. It is reasonable to use the organosilicon phenols as modifiers of organic resins and compositions for adding properties of heat and frost resistance, water repellency, etc. to organoelemental and organic materials [2-4]. A method for production of organosiloxane phenolic resins based on the products of high-temperature condensation of alkoxysilanes and siloxanes with organic bisphenols has been claimed [5]. A synthesis of copolymers by polycondensation of organosilicon phenols with organic hydroxymethylphenols was reported [6]. The (hydroxymethyl)hydroxyphenyldimethylsiloxanes containing both phenol and hydroxymethyl functional groups have been described [7].

In this paper we discuss the features of the method of synthesis and properties of carbofunctional (hydroxymethyl)hydroxyphenyldimethylsiloxanes of linear and branched structure. The presence in their structure of hydroxymethyl and phenol reactive groups enhances their performance as a source reagents for the synthesis of copolymers and modifiers of organic polymers.

Synthesis of (hydroxymethyl)hydroxyphenyl-dimethylsiloxanes was performed by hydroxymethylation of the organosilicon phenols [4] of general formula R'[Si(CH₃)₂O]_n[Si(CH₃)RO]_mSiMe₂R', where R' is 4-hydroxy-3-methoxyphenylpropyl group, R is methyl or 4-hydroxy-3-methoxyphenylpropyl group, with formaldehyde in aqueous alkaline medium.





The *para*- and *ortho*-positions relative to the OH group in the phenyl radical of the source phenol are occupied by propylsilyl and methoxyl substituents, respectively. Therefore, the hydroxymetylation is possible only at the unoccupied *ortho*-position in the phenol fragment. The optimum conditions of the synthesis are pH 10–11 and temperature from +35 to +45°C. At pH <

10 the reaction proceeds slowly. At pH > 12 and at higher temperatures the process is complicated by the polycondensation reaction. As a result a series of monomers and oligomers differing by the lengths of siloxane chain and the location of 3-[4-hydroxy-3-(hydroxymethyl)-5-(methoxyphenyl)]propyl substituent was obtained:



The products of hydroxymethylation are dark yellow liquids of different viscosity, well soluble in chlorinated hydrocarbons, toluene, and ethanol. The structure of compounds **I–IV** was confirmed by NMR and IR spectroscopy and elemental analysis. The NMR spectra indicate the presence of proton

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¹H NMR spectrum of (a) compound **IV** and (b) initial phenol.

Group	δ, ppm		
Si–CH ₃	0.00-0.16		
Si-CH ₂ ¹ -CH ₂ ² -CH ₂ ³	0.45-0.65 (CH ₂ ¹), $1.54-1.75$ (CH ₂ ²),		
	2.45–2.66 (CH ₂ ³)		
H_3^1CO H^5	3.70-3.85 (CH ₂ ¹), 5.45-5.55 (CH ₂ ²),		
	5.45-5.55 (CH ₂ ³), 4.60-4.74 (CH ₂ ⁴),		
H ² O	6.75–6.79 (CH ₂ ⁵)		
$H^{3}O-H_{2}^{4}C$ H^{5}			
H^1 H	7.00–7.10 (CH ¹)		
но			
HOH ₂ C H			

Table 1. Chemical shifts in the ¹H NMR spectra of (hydroxymethyl)hydroxyphenylorganosiloxanes

signals with chemical shifts characteristic of hydroxymethyl group (see Table 1 and the figure). The IR spectroscopy data show that while the absorption band of the phenol OH group in the spectrum of the initial organosilicon phenol falls into the region of 3513 cm^{-1} , in the spectra of (hydroxymethyl)hydroxyphenyldimethylsiloxanes the presence of hydroxymethyl groups leads to the shift of the OH absorption band to the region of 3375 cm^{-1} . The properties of the synthesized compounds are listed in Table 2.

δ, ppm

Table 2 shows that the values of dynamic viscosity of compounds I and III are 1925 and 177 cP, respectively, while those of the original phenols are respectively 910 and 60 cP. Higher viscosity of the (hydroxymethyl)hydroxyphenyldimethylsiloxanes compared to the initial phenols may be related to the formation of additional hydrogen bonds due to the presence of the CH₂OH groups.

Comp. no.	Name	$d_{\rm r} {\rm ~g~cm^{-3}}$	M, g mol ⁻¹	$n_{\rm D}^{20}$	μ, cP
Ι	1,3-Bis-[3-(4-hydroxy-3-hydroxymethyl-5-methoxyphenyl)propyl]- tetramethyldisiloxane	1.09	523	1.5200	1925
Π	α, ω -Hexamethyl-octa-[3-(4-hydroxy-3-hydroxymethyl-5-methoxy-phenyl)propyl]oligodimethylsiloxane 8/32	1.070	4562	1.4630	3605
III	α, ω -Bis-[3-(4-hydroxy-3-hydroxymethyl-5-methoxyphenyl)propyl]- oligodimethylsiloxane-30	1.01	2594	1.4270	177
IV	1,1,1,2,3,3,3-Heptamethyl-2-[3-(4-hydroxy-3-hydroxymethyl-5- methoxyphenyl)propyl]trisiloxane	1.029	416	1.4875	230

Table 2. Some characteristics of organosilicon hydroxymethylphenols

By an example of compound IV we investigated the condensation of the hydroxymethylated compounds at the CH_2OH groups proceeding at heating. It is confirmed by the ¹H NMR spectroscopy that at heating to 150°C occurs the formation of ether bonds – CH_2 –O– CH_2 – (s, δ 4.75 ppm), and then at the temperature above 200°C, methylene bridges (s, δ 4.71 ppm) similarly to [8].



Compound IV with one hydroxymethyl group in the molecule can form only a dimer, while compounds I and III, containing two CH_2OH group, at heating to 150–200°C form soluble linear condensation products.

Investigation of the product of polycondensation of compound I by size-exclusion chromatography showed that it is an oligomeric compound comprising molecules differing by the degree of polycondensation,

	Temper				
Material	5%	20%	50%	Residue at 800° C, wt %	
Rezite	366	525	631	31.2	
Rezite + 5% of modifier	388	556	648	41.7	
Rezite + 10% of modifier	390	563	652	46.6	

Table 3. Thermogravimetric analysis of resites based on phenol-formaldehyde resin and compound II

with molecular masses in the range 1078-6046 g mol⁻¹. The molecular-mass characteristics of the product of polycondensation of compound I also confirm that it has a broad polydispersity:

Mn	Mw	Mz	Mw/Mn	Content, %
870	7500	45500	8.62	98.5

The multifunctional compound **II** on heating at 150°C for 20 min affords a polycondensation product, which is soluble in toluene, chloroform, and isopropyl alcohol. Raising the temperature to 200°C and keeping the sample for 20 min produces a substance insoluble in these solvents. This can be explained by deeper condensation and, consequently, cross-linking of the oligomer with the formation of methylene bridges.

The synthesized compounds were used also as modifiers of organic polymer by an example of phenol-formaldehyde resins of resol type, obtained by the procedure [9]. We selected as the modifier compound II. Modification of phenol-formaldehyde resin with the (hydroxymethyl)hydroxyphenyldimethylsiloxane should proceed through the co-condensation of hydroxymethyl groups of organic and organosilicon oligomers to form a block copolymer. We prepared three compositions: individual resol, and the resols containing 5% and 10% by weight of hydroxymethylated oligosiloxane. These compositions were heated at 200°C for 1 h. Analysis of the modified products showed content of the sol-fraction in them of 1% by weight. This confirms the high level of formation of the copolymer with three-dimensional structure.

To assess the thermal stability of the obtained compositions we carried out the thermogravimetric analysis of the obtained resites in air (Table 3).

As can be seen, the modified samples are by 20– 30°C more stable thermally compared with the unmodified ones.

Modification of phenol-formaldehyde resin with (hydroxymethyl)hydroxyphenyldimethylsiloxanes also

leads to an increase in the glass transition temperature of the samples from 146 to 160°C.

EXPERIMENTAL

The IR spectra were recorded on a Vector-22 Bruker FTIR spectrometer in the range v 400– 4000 cm⁻¹. The gel-permeation cromatography was performed on an instrument from Knauer company, with a refractometric detector, Stirogel column, and THF as eluent. The NMR data were obtained on a Bruker AT 360 MHz NMR spectrometer.

The thermogravimetric analysis was performed on a Perkin Elmer TGS-2 termoanalyzer, heating rate 10°C min⁻¹, temperature range 40-800°C. The measuring of the glass transition temperature (dilatometric analysis) was performed on the same Perkin Elmer TGS-2 termoanalyzer, heating rate 5°C min⁻¹, temperature range 50-250°C. Sample dimensions: height 1-1.5 mm, width 2-3mm. The diameter of the flat end of a quartz rod of the measuring device 3.5 mm. The preliminary calibrated chrome-aluminum thermocouple is located at the 1-1.5 mm distance from the sample. The load required for the desired contact of the rod with the sample 1 g. The transition from the glassy to the viscoelastic state is displayed on the plot of the size (height) of the sample on temperature as a jump in the narrow temperature range. As the T_g is adopted the point of intersection of the tangents to the curve branches.

Dynamic viscosity was measured on a Brookfield DV-E viscometer, no. 28 spindle, rotation speed 100 rpm. The tested oligomer is poured into a steel cup to the mark, the cup is fixed in thermally controlled jacket. The rotation speed is set after the temperature stabilization.

1,3-Bis-[3-(4-hydroxy-3-hydroxymethyl-5-methoxyphenyl)propyl]tetramethyldisiloxane (I). The reaction flask equipped with a thermometer, a reflux condenser and a stirrer, was charged with 4.86 of NaOH and 3.781 ml of water, and 50.1711 g of α,ω bis-[3-(4-hvdroxy-3-methoxyphenyl)propyl]tetramethyldisiloxane was added dropwise with stirring. After the viscous mass formation, 133 ml of 37% aqueous solution of formaldehyde was added. The reaction mixture was stirred at 40°C for 4 h, then 10.98 ml of 35% aqueous HCl was added. After separation of layers, the reaction mixture was diluted with 100 ml of CHCl₃. The lower layer, the solution of the reaction product in CHCl₃, was seprated in a separating funnel from the upper water layer, and washed with water to pH 7. The solvent, water, and the remaining CH₂O were distilled off at 60°C (133 Pa) on a rotary evaporator. 53.6 g (95% yield) of 1,3-bis-[3-(4-hydroxy-3-hydroxymethyl-5-methoxyphenyl)propyl]tetramethyldisiloxane was obtained. Found, %: C 61.52, H 8.82, Si 11.17. C₃₂H₄₂O₇Si₂. Calculated, % C 59.73, H 8.1, Si 10.74.

α,ω-Hexamethylocta-[3-(4-hydroxy-3-hydroxymethyl-5-methoxyphenyl)propyl]oligodimethylsiloxane 8/32 (II) was prepared analogously to compound I. Yield 94% (38.78 g). Found, %: C 3.82, H 8.15, Si 26.81. $C_{166}H_{354}O_{65}Si_{42}$. Calculated, % C 3.64, H 7.56, Si 25.78.

 α, ω -Bis-[3-(4-hydroxy-3-hydroxymethyl-5methoxyphenyl)propyl]oligodimethylsiloxane-30 (III) was prepared analogously to compound I. The yield of product III 96% (26.98 g). Found, %: C 2.53, H 7.31, Si 33.98. C₈₂H₂₁₀O₃₅Si₃₀. Calculated, % C 2.39, H 7.17, Si 32.38.

1,3-Hexamethyl-2-methyl-2-[3-(4-hydroxy-3-hydroxymethyl-5-methoxyphenyl)propyl]trisiloxane (IV) was prepared analogously to compound I. Yield 94% (48.0 g). Found, %: C 54.47, H 8.54, Si 21.03. $C_{18}H_{36}O_5Si_3$. Calculated, % C 51.88, H 8.71, Si 20.22.

Condensation of compound I. A fluoroplastic mold charged with 3.3 g of 1,3-bis-[3-(4-hydroxy-3-hyd-roxymethyl-5-methoxyphenyl)propyl]tetramethyldi-siloxane was placed in a vacuum oven and heated at 200°C for 60 min, then cooled to room temperature. The resulting product was a resinous plastic homo-

geneous transparent mass of dark amber color, soluble in toluene, chloroform, and aliphatic alcohols.

Preparation of compositions based on the phenol-formaldehyde resins. A phenol-formaldehyde resin of resol type was divided into three portions, which were placed in glass cups. To two samples was added 0.8 g (5 wt %) and 1.6 g (10 wt %), respectively, of compound II at continuous stirring.

For the preparation of 5% modified rezite, the fluoroplastic mold was filled with 3 g of 5% of the modified resol, the mold was placed in a vacuum oven and heated at 120°C for 60 min. Then temperature was raised to 200°C and heating was continued for 60 min. After cooling to room temperature, a product as an opaque solid glassy mass insoluble in ethanol was obtained. Analysis for the gel fraction showed the presence in the condensation product of 1% of ethanol-soluble substances.

The 10% modified rezite was prepared similarly. Analysis showed the presence in the condensation product of 1% of sol fractions.

REFERENCES

- Sergeev, V.A., Shitikov, V.K., Abbasov, G.U., Bairamov, M.R., and Zhdanov, A.A., *Vysokomol. Soedin., A*, 1987, vol. 29, p. 2441.
- 2. US Patent no. 4923912, 1990.
- 3. JP Patent no. 63199220, 1988.
- 4. RF Patent no. 2211845, 2001.
- 5. Germany Patent no. 937555, 1956.
- 6. Greber, G., Angew. Makromol. Chemie, 1968, vol. 4, no. 41, p. 212.
- 7. RF Patent no. 2397994, 2010.
- Slonim, I.Ya. and Urman, Ya.G., *YaMR-spektroskopiya* geterotsepnykh polimerov (NMR Spectroscopy of Hetero-Chain Polymers), Moscow: Khimiya, 1982, p. 173.
- 9. Nikolaev, A.F., *Tekhnologiya plasticheskikh mass* (Technology of Plastics), Leningrad: Khimiya, 1977, p. 174.