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Synthesis and Investigation of Organosilicon Dendrimers Based on Octavinylsilsesquioxane and Sulfenyl Chlorides of Metal Acetylacetonates

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Abstract—The addition of sulfenyl chlorides of metal acetylacetonates to octavinylsilsesquioxane was studied. The addition was shown to proceed at four of the eight vinyl groups of the octavinylsilsesquioxane, without the formation of cross-linked polymers. This allowed us to synthesize with high yields new non-functianalized and functianalized dendrimers based on octavinylsilsesquioxane and the sulfenyl chlorides of metal acetylacetonates.

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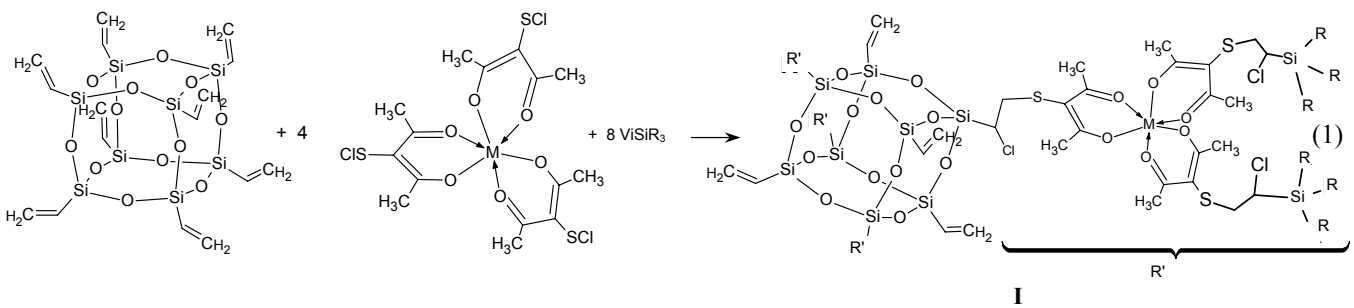
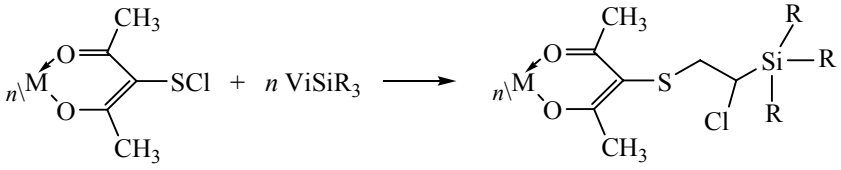
Recently a great interest is directed to the synthesis of compounds with a desired spatial structure, including dendrimers based on organosilicon compounds [1–3]. In this study we investigated the reaction of sequential addition of sulfenyl chlorides of metal acetylacetonates and triethyl- or trietoxyvinylsilane to octavinylsilsesquioxane, according to scheme (1). Complexes of Cr(III), Co(III), Al(III), and Be(II) were involved in the reaction.

Compound **I** was isolated using gel chromatography on a column packed with a styrene–divinylbenzene copolymer in a medium of dry toluene. At the ratio of reagents octavinylsilsesquioxane: $M(AcAcSCl)_3$ equal to 1:10 and 1:8 the chromatograms showed the presence of a mixture of two substances, while at the ratio of 1:4 a single reaction product formed. Substances formed with lower yield, that is, with higher molecular weight, contain according to the solid-state ^{29}Si NMR spectroscopy the signals of the silicon atoms of the octasilsesquioxane and triethylsilyl fragments. The second product showed the signals of silicon atoms only of triethylsilyl fragment. The theoretical calculation of the masses of the substances formed in the reaction, their comparison with the results of gel-permeation chromatography, that is, with



M = Cr(III), Co(III), Al(III); R = Et, OEt; $ViSiR_3$ = CH=CHSiEt$_3$, CH=CHSi(OEt)$_3$.

the masses of the practically isolated substances, and the data of elemental analysis, ^{29}Si and ^{13}C NMR and IR spectroscopy, allowed us the following conclusion. The sulfenyl chlorides of acetylacetonates of Cr(III), Co(III), Al(III), and Be(II) add to the octavinylsilsesquioxane at four of the eight vinyl groups. The addition reaction proceeds quantitatively in two steps according to reaction (1) with the formation of dendrimer of the structure **I**. At the initial ratio of reactants octavinylsilsesquioxane:$M(AcAcSCl)_3$ 1:8 or 1:10 the second product is formed from the sulfenyl chloride acetylacetonate, unreacted with octavinylsilsesquioxane, and vinyltriethyl- or vinyltriethoxysilane, respectively (2):



(2)

^{29}Si, ^{13}C NMR, IR spectroscopy, and elemental analysis data

Compound	Substituent	NMR spectrum, δ, ppm		IR spectrum, ν, cm^{-1}		Found, %	Formula	Calculated, %
		^{13}C	^{29}Si	Si–O	$C{=}O_{chelate}$			
$(CH_2CHSiO_{1.5})_8$		138.92, 129.67	–80.04, –80.47	1111	–	C 29.75; Si 34.53	$C_{16}H_{24}O_{12}Si_8$	C 30.38; Si 35.44
Ia	M = Cr, R = Et	–	–	1120	1552	C 41.83; S 10.07; Cl 9.97; Si 11.12; Cr 5.01	$C_{140}Cl_{12}Cr_4H_{240}O_{36}S_{12}Si_{16}$	C 42.39; S 9.70; Cl 10.72; Si 11.33; Cr 5.24
Ib	M = Al, R = Et	139.46, 197.96, 104.83, 28.08, 4.19, 8.38, 38.40, 45.40	9.00, –74.24, –78.74	1122	1568	C 44.15; S 9.83; Cl 11.58; Si 11.41	$Al_4C_{140}Cl_{12}H_{240}O_{36}S_{12}Si_{16}$	C 43.49; S 9.95; Cl 11.00; Si 11.62
Ic	M = Be, R = Et	138.06, 198.43, 105.3, 27.14, 4.21, 8.42, 38.37, 45.39	9.25, –74.1, –77.93	1122	1558	C 40.74; S 10.66; Cl 11.35; Si 13.11	$Be_4C_{88}Cl_8H_{144}O_{28}S_8Si_{12}$	C 41.25; S 10.00; Cl 11.09; Si 13.13
Id	M = Cr, R = OEt	–	–	1104	1552	C 37.98; S 9.14; Cl 10.42; Si 10.25; Cr 4.65	$C_{140}Cl_{12}Cr_4H_{240}O_{60}S_{12}Si_{16}$	C 38.65; S 8.83; Cl 9.80; Si 10.31; Cr 4.79
Ie	M = Al, R = OEt	138.38, 129.94, 197.44, 104.06, 28.13, 19.13, 60.19, 39.94, 44,44	–57.68, –73.86, –78.21	1104	1570	C 40.23; S 9.76; Cl 10.74; Si 10.32	$Al_4C_{140}Cl_{12}H_{240}O_{60}S_{12}Si_{16}$	C 39.57; S 9.04; Cl 10.03; Si 10.55
If	M = Be, R = OEt	139.92, 129.11, 198.18, 105.58, 27.26, 19.04, 60.15, 39.38, 46.30	–57.92, –74.33, –78.45	1104	1560	C 38.08; S 10.21; Cl 11.07; Si 11.89	$Be_4C_{88}Cl_8H_{144}O_{40}S_8Si_{12}$	C 38.37; S 9.30; Cl 10.32; Si 12.21

This course of reaction (1) with the quantitative yields is due to much slower addition of next sulfenyl chloride groups of the metal acetylacetonate sulfenyl chloride molecules. Most likely, the addition occurs only through a single silicon atoms in the octavinylsilsesquioxane molecule, as reflects structure **I** in scheme (1).

All the dendrimers with the composition and structure of **I** have been isolated and characterized by physicochemical methods (^{29}Si, ^{13}C NMR and IR spectroscopy and elemental analysis, see the table). These compounds are first-generation dendrimers based on octavinylsilsesquioxane and sulfenyl chlorides of metal acetylacetonates with functionality 24 [M = Cr(III), Co(III), and Al(III)] and 12 [M = Be(II)] (the number of ethoxy or ethyl end groups).

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