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Organosilicon Polymers Based on Polyvinylsilsesquioxane and Sulfenyl Chlorides of Metal Acetylacetonates

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Abstract—Addition of sulfenyl chlorides of metal acetylacetonates to poly(vinylsilsesquioxane) followed by addition of vinyltributylsilane has yielded polymers containing metal chelate fragments. The metal complex addition has been studied at varied ratio of the reagents; the highest reached conversion of vinyl groups is 60%.

Keywords: organosilicon compound, poly(vinylsilsesquioxane), acetylacetonate, branching

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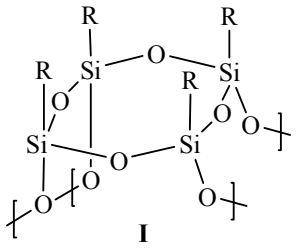
Branched polymers, including hyperbranched ones and dendrimers [1] have become popular objects in polymer science over the last two decades.

In this work we studied sequential additions of sulfenyl chloride derivatives of metal acetylacetonate and of vinyltributylsilane to the cyclolinear poly(vinylsilsesquioxane) **I**.



I

R = CH=CH$_2$.

The poly(vinylsilsesquioxane) **I** was prepared via polycondensation of 80.7 g (0.5 mol) of vinyltrichlorosilane and 250 g (13.9 mol) of water as described elsewhere [3]; the yield was 97%. The polycondensation product structure was studied previously by means of X-ray photoelectron spectroscopy, X-ray diffraction, and positron diagnostics [4, 5]. Molecular mass of polymer **I** could not be determined precisely; according to the gel permeation chromatography data it was estimated as below 5000.

The polymer **I** was further modified with the branched side groups. The modification involved two stages.

Firstly, the solution of polymer **I** in toluene was added to the solution of tris(acetylacetonato) metal(III) modified with sulfenyl chloride groups (the metal was chromium, cobalt, or aluminum).

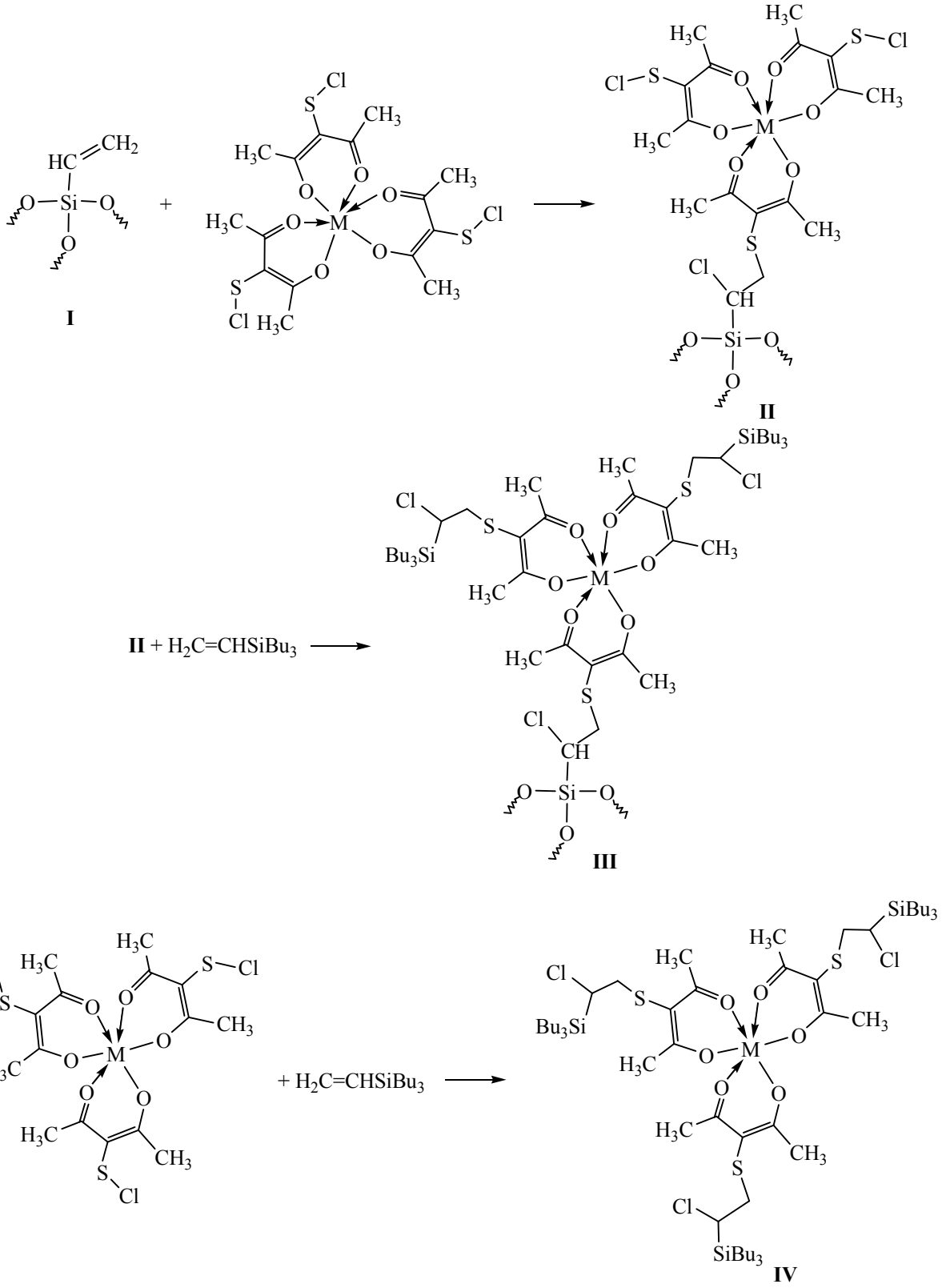
The molar ratio of the metal complex and the polymer **I** vinyl groups was 1 : 1, 2 : 1, 3 : 1, or 4 : 1. The applied order of the reagents mixing and excess of the metal complex suppressed the network formation. The so prepared reaction mixture was introduced into the second stage of the modification by addition of excess of vinyltributylsilane. The latter acted as the protective group to block the residual sulfenyl chloride fragments (Scheme 1).

Product **III** was isolated by gel chromatography using cross-linked polystyrene as the sorbent and anhydrous toluene as the eluent. According to the chromatography and the elemental analysis data (see the table), the reaction mixtures contained two types of products: the target polymer **III** and the adduct **IV** of vinyltributylsilane with the excess of the metal complex introduced in the first stage of modification (Scheme 1).

The products could not be separated and identified by thin layer chromatography, as they were irreversibly bound to the sorbent and further decomposed.

IR spectra of the isolated products **III** contained the following absorption bands (cm^{-1}): 1552 [assigned to ν(C=O) of the γ-substituted chelate cycle], 1411 (vinyl group), 1134 [ν(Si–O) of the polyvinylsiloxane

Scheme 1.



Elemental analysis data of the starting polyvinylsilsesquioxane **I** and the products **III** and **IV** prepared at the reagents ratio of 4 : 1

Product	Found, %					Yield, %	Calculated, %				
	Si	C	H	S	Cl		Si	C	H	S	Cl
I	34.8	30.1	4.0	–	–	97	35.5	30.4	3.8	–	–
III-Cr	9.3	47.8	7.5	8.4	9.5	96	9.1	49.1	7.4	8.5	9.4
III-Al	9.2	50.5	7.7	8.5	9.7	93	9.3	50.2	7.5	8.7	9.6
III-Co	9.1	49.2	7.5	8.1	9.5	94	9.0	48.8	7.3	8.4	9.3
IV-Cr	3.4	44.2	5.9	12.1	13.9	97	3.6	44.9	6.2	12.4	13.7
IV-Al	3.1	47.1	6.1	12.5	14.5	96	3.7	46.4	6.4	12.8	14.2
IV-Co	3.3	45.1	6.5	11.9	13.8	93	3.6	44.5	6.2	12.3	13.6

fragment], and ≈3000 [a group of bands assigned to the ν(C–H) vibration of the aliphatic methyl, methylene, and methine groups].

We compared theoretical yields of the products with those determined experimentally (collected in the table). It was found that addition of the metal complex to the polyvinylsilsesquioxane at the stage of the product **II** formation occurred at only one of the three S–Cl groups of the complex. With the initial ratio of the metal complex and vinyl groups of the polymer **I** of 1 : 1, 2 : 1, 3 : 1, and 4 : 1, the fraction of the modified vinyl groups was 44, 53, 59, and 60%, respectively. Hence, the conversion of vinyl groups was apparently limited by steric hindrance caused by the bulky metal complex substituents, and further increase of the metal complex excess did not increase the polymer **I** conversion into the products.

ACKNOWLEDGMENTS

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REFERENCES

1. Teertstra, S.J. and Gauthier, M., *Prog. Polym. Sci*., 2004, vol. 29, no. 4, p. 277. DOI: 10.1016/j.progpolymsci.2004.01.001
2. Kul'chin, Yu.N., Voznesenskii, S.S., Dzhuba, V.P., Shcherbakov, A.V., Shapkin, N.P., Tutov, M.V., and Bazhenov, V.V., RF Patent 2424244, 2011.
3. Alikovskii, A.V. and Krasitskaya, S.G., *Russ. J. Gen. Chem.,* 2010, vol. 80, no. 2, p. 245.
4. Vovna, V.I., Os'mushko, I.S., Korochentsev, V.V., Shapkin, N.P., and Tutov, M.V., *J. Struct. Khim*., 2010, vol. 51, no. 5, p. 875.
5. Shapkin, N.P., Kul'chin, Yu.N., Razov, V.I., Voznesenskii, S.S., Bazhenov, V.V., Tutov, M.V., Stavnistyi, N.N., Kuryavyi, V.G., and Slobodyuk, A.B., *Russ. Chem. Bull*., 2011, vol. 60, p. 1640. DOI: 10.1007/s11172-011-0245-1.