REVIEWS

Carbofunctional Sulfur-Containing Organosilicon Compounds: Synthesis and Application Fields

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Abstract—Recently published data concerning the preparation and valuable properties of organosilicon compounds of silatrane structure with carbofunctional sulfur-containing substituents (thiol, sulfide, disulfide, polysulfide) and heteroatomic sulfur-containing groups (thiourea, thiourea dioxide, dithiocarbamate, thiuram disulfide) are summarized and analyzed.

The first few data concerning chemistry of carbofunctional sulfur-containing organosilicon compounds were summarized in 1985 by Voronkov and Vlasova [1], who actually initiated systematic study of this class of organosilicon compounds. Their studies gave rise to a new field of organosilicon chemistry: synthesis and study of organosilicon ion-exchange and complexing sorbents [2].

Data published in the past 15 years on the chemistry of carbofunctional organosilicon compounds demonstrate wide use of these compounds as modifying and cross-linking agents, vulcanizers, adhesives, and additives to elastomers and polymer compounds, imparting to them thermal plasticity, lightfastness, heat resistance, etc. The preparation procedures, structural features, and reactivity of organosilicon compounds of this type are described to a considerably lesser extent.

A procedure for preparing thiols of the general formula $R_2(R^1O)SiR^2SH$ [$R = C_{1-8}$-alk(en)yl, aryl, aralkyl (mainly R = Me, Et); $R^1 = C_{1-24}$-alkyl, alkenyl, aryl (mainly R^1 = Et); $R^2 = C_{1-30}$-alkylene, organylene (mainly $R^2 = -CH_2CH_2CH_2-$)] in mixtures with the corresponding sulfides and polysulfides is based on the reaction of halogenated silanes $R_2(R^1O)SiR^2X$ (X = halogen) with sodium or potassium hydrosulfide hydrate $MSH \cdot H_2O$, powdered alkali metal carbonates $M_2^1CO_3$, and powdered elemental sulfur in the approximate ratio halosilane : S : MSH : $M_2^1CO_3$ = 1 : 0.6 : 1.1 : 0.7 in an alcoholic solution [3].

Organosilicon compounds of the general formula $GC(O)SCH_2CH_2CH_2SiX_3$, where X = OR or R, R = H or alkyl group containing (or not containing) unsaturated alkenyl, aryl, or aralkyl fragments, the number of RO groups is ≥1, and G is a univalent alkyl group, were prepared and suggested as binding agents for filled rubber compounds and items [4]. For example, 3-(trimethoxysilyl)-1-propyl S-acetothioate was synthesized by the reaction of 3-(trimethoxysilyl)-1-propanethiol with acetic anhydride at 155–225°C in more than 90% yield:

$$(CH_3O)_3SiCH_2CH_2CH_2SH \xrightarrow{4(CH_3CO)_2O} (CH_3COO)_3SiCH_2CH_2CH_2SCOCH_3 + 3CH_3COOMe + CH_3COOH. \qquad (1)$$

New types of organosilicon biologically active compounds based on organosilicon alkanethiols have been described [5]. For example, the reaction of 3-mercaptopropyl(trimethoxy)- and 3-mercaptopropyl(triethoxy)silanes with the titanium complex [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$] (1) in the presence

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of triethylamine yielded titanium thiolate complexes [Ti(η^5-C$_5$H$_5$)$_2$\{SCH$_2$CH$_2$CH$_2$Si(OMe)$_3$\}$_2$] (2) and [Ti(η^5-C$_5$H$_5$)$_2$\{SCH$_2$CH$_2$CH$_2$Si(OEt)$_3$\}$_2$] (3). Grafting of titanium complexes 1–3 to dehydroxylated silica gel MCM-41 yielded new organosilicon materials MCM-41/[Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$] (S1), MCM-41/[Ti(η^5-C$_5$H$_5$)$_2$\{SCH$_2$CH$_2$CH$_2$Si(OMe)$_3$\}$_2$] (S2), and MCM-41/[Ti(η^5-C$_5$H$_5$)$_2$\{SCH$_2$CH$_2$CH$_2$Si(OEt)$_3$\}$_2$] (S3).

The anticancer activity of nonfunctionalized silica gel MCM-41 and of hybrid substances S1–S3 toward such cells as adenocarcinoma HeLa, human myelogenic leukemia K562, and malignant melanoma Fem-x was studied. Studies have shown that nonfunctionalized silica gel MCM-41 is inactive toward all the tested types of cancer cells, whereas its functionalized derivatives S1–S3 efficiently acted on all the above human cancer cells. The cytotoxicity of compounds S2 and S3 toward all the kinds of malignant tumors was virtually equal. Compound S1 appeared to be the least active. The new class of organosilicon materials obtained can be used as bone filler or as additive to a bone implant.

A rubber compound [6] containing hydrophobized silica and siloxane-functionalized styrene–butadiene rubber was developed as material for tires with high high-strength protectors. Hydrophobized silica was modified with alkoxyorganomercaptosilanes or bis(3-ethoxysilylpropyl) polysulfide.

Organosilicon thiols of the general formula X$_3$Si(CH$_2$)$_n$SH [X = MeO, C$_2$H$_5$O, and/or CH$_3$CO, n = 0–3] were recommended, among other carbofunctional organosilicon compounds, as binding agents for formulations for oil well cleaning [7]. The same thiols in combination with styrene, methacrylates, alkyl acrylates, and alkenylcarboxylic acids were suggested as binding agents for preparing stone-imitating coatings [8]. These coatings exhibit low glass transition point, very low film formation point, and good antimud properties owing to strong shell.

An effective cross-linking agent, bis[3-(triethoxysilyl)-propyl] disulfide, was prepared by high-temperature reaction of (3-mercaptopropyl)triethoxysilane with sulfur [9]. The advantages of this synthesis pathway are simplicity, short reaction time under relatively mild con-

ditions, and absence of by-products. This procedure opens wide prospects for commercial production of the high-quality organosilicon polysulfide cross-linking agent.
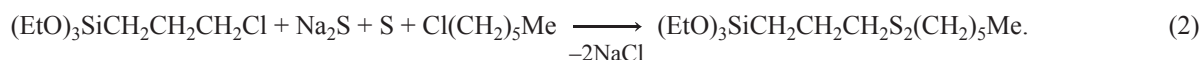
A new procedure was suggested for preparing organosilicon nanoparticles from organosilicon compounds containing thiol and amino groups [10]. (3-Mercaptopropyl)trimethoxysilane (MPTMS) and (3-aminopropyl)trimethoxysilane (APTMS) are used as precursors. They are involved in acid-catalyzed polycondensation in a water-soluble organic solvent, e.g., dimethyl sulfoxide. The critical content of APTMS in the silane mixture whose hydrolysis yields stable nanoparticles is no more than 25%, and the lowest APTMS content sufficient for the formation of stable nanoparticles approximately 200 nm in diameter is 1%. The cationic nanoparticles obtained can bind antisense oligonucleotides in a composition-dependent manner.

Organosilicon compounds containing a sulfide or polysulfide moiety in the organic radical are still of much practical interest. For example, organosilicon polysulfides of the general formula (RO)$_3$Si(CH$_2$)$_x$SS$_z$(CH$_2$)$_x$Si(OR)$_3$ (R = C$_{1-8}$-alkyl, x = 2–6, z = 0–6) are suggested as additives for production of vulcanized rubber [11], and polysulfides (RO)$_3$Si(CH$_2$)$_3$S$_x$(CH$_2$)$_3$Si(OR)$_3$ (x = 2–2.4, fraction with x = 2 $\geq$75%), as one of components for production of moisture- and wear-resistant tires of low combustibility [12].

The majority of methods for preparing organosilicon sulfides and polysulfides are based on using organosilicon chlorides and bromides as starting compounds. For example, high-purity organosilicon polysulfides of type (R^{1}O)$_3$SiR$_2$S$_x$R^{2}Si(OR^1) were prepared by the reaction of sulfur and alkali metal with (R^{1}O)$_3$SiR^{2}X, where X = Cl or Br.

Similarly, a mixture of polysulfides of the general formula [(EtO)$_3$Si(CH$_2$)$_3$]$_2$S$_x$ with the mean number of sulfur atoms of 2.6 was obtained in 92% yield by the reaction of 3-chloropropyl(triethoxy)silane with sodium polysulfide. The latter was synthesized from sodium metal and elemental sulfur at 140°C in xylene [13].

The disulfide (EtO)$_3$Si(CH$_2$)$_3$S$_2$(CH$_2$)$_5$Me was prepared by the reaction of a mixture of 3-(chloropropyl) triethoxysilane and hexyl chloride with sodium sulfide in the presence of elemental sulfur [14]:
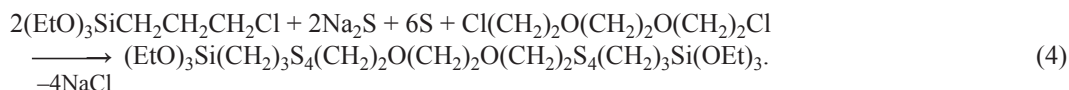
$$(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{Na}_2\text{S} + \text{S} + \text{Cl}(\text{CH}_2)_5\text{Me} \xrightarrow[-2\text{NaCl}]{} (\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{S}_2(\text{CH}_2)_5\text{Me}. \quad (2)$$

The tetrasulfide $(EtO)_3Si(CH_2)_3S_4(CH_2)_2O(CH_2)_2OH$ was prepared by the reaction of (3-chloropropyl)-triethoxysilane with sodium sulfide, elemental sulfur, and monochlorodiethylene glycol [15]:
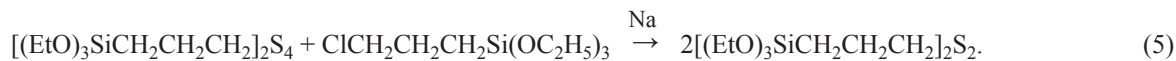
$$(EtO)_3SiCH_2CH_2CH_2Cl + Na_2S + 3S + Cl(CH_2)_2O(CH_2)_2OH \xrightarrow{-2NaCl} (EtO)_3SiCH_2CH_2CH_2S_4(CH_2)_2O(CH_2)_2OH. \quad (3)$$

Similar reaction involving (3-chloropropyl)-triethoxysilane and dichlorotriethylene glycol yielded the symmetrical tetrasulfide $(MeO)_3Si(CH_2)_3S_4(CH_2)_2O \cdot (CH_2)_2O(CH_2)_2S_4(CH_2)_3Si(OMe)_3$ [16]:

$$2(EtO)_3SiCH_2CH_2CH_2Cl + 2Na_2S + 6S + Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$$
$$\xrightarrow{-4NaCl} (EtO)_3Si(CH_2)_3S_4(CH_2)_2O(CH_2)_2O(CH_2)_2S_4(CH_2)_3Si(OEt)_3. \quad (4)$$

A procedure for preparing organosilicon polysulfides, promising as agents binding rubber with silica for the development of silica-filled tires, has been patented [17, 18]. In particular, bis(3-triethoxysilylpropyl) disulfide was prepared in high yield by the reaction of bis(3-triethoxysilylpropyl) tetrasulfide with 3-chloropropyl(triethoxy)silane in the presence of sodium metal at 60°C:

$$[(EtO)_3SiCH_2CH_2CH_2]_2S_4 + ClCH_2CH_2CH_2Si(OC_2H_5)_3 \xrightarrow{Na} 2[(EtO)_3SiCH_2CH_2CH_2]_2S_2. \quad (5)$$

Similar procedure for preparing organosilicon polysulfides was used in [19–21], with the only difference that the reaction was performed in the presence of a phase-transfer catalyst. For example, the procedure for preparing organosilicon polysulfides of the general formula $(RO)_{3-m}R_mSi–Alk–S_n–Alk–SiR_m(OR)_{3-m}$, where R is a univalent hydrocarbon radical containing 1–12 carbon atoms, Alk is a bivalent hydrocarbon radical containing 1–18 carbon atoms, $m = 0–2$, and the mean value of n is in the range 2–8, involves in the first step the formation of sodium polysulfide by heating elemental sulfur with MSH or M_2S (M = NH_4, Na, K) at 90–100°C [22]. The sodium polysulfide obtained is condensed with halogenated organosilicon compounds $(RO)_{3-m}R_mSi–AlkX$ (X = Cl, Br, I) in the presence of a phase-transfer catalyst such as tetrabutylammonium chloride, bromide, etc. Generally, phase-transfer catalysts are widely used in synthesis of organosilicon polysulfides [23–28]. All these procedures do not differ from each other essentially. In virtually all the procedures, the starting sulfiding agents are hydrosulfides, sulfides, and polysulfides of ammonium or alkali metals. These compounds, as a rule, are brought into the reaction with 3-chloropropyl(trialkoxy)silane $ClCH_2CH_2CH_2Si(OR)_3$. Quaternary ammonium salts, most frequently tetrabutylammonium bromide, are used in all the studies as phase-transfer catalysts. In most cases, the final reaction product is a mixture of organosilicon polysulfides with the sulfide chain containing from two to five sulfur atoms. Nevertheless, variation of the process conditions allowed the development of procedures for preparing individual bis[3-(trimethoxysilyl)-propyl] disulfide [27] and bis[3-(trimethoxysilyl)propyl]tetrasulfide [28] suggested as cross-linking agents. The process for preparing sulfur-containing organosilicon compounds, based on phase-transfer catalysis, allows preparation of target products of enhanced stability and high purity. Under these conditions, the formation of hydrogen sulfide as by-product is reduced to a minimum or avoided at all.

A composite with good stability of the viscosity coefficient in the course of storage for 3 weeks at 35°C and relative humidity of 75% was prepared by mixing Hisil 233 with stearic acid, polysulfide $(R^1O)_3SiR^2S_xR^2Si(OR^1)_3I$ [R^1 = Et, R^2 = $(CH_2)_3$, $x = 4$], and ZnO [29].

An interesting method was suggested for preparing unsaturated organosilicon sulfides of the general formula $(R^1O)_3SiCH=CH(CH_2)_nSR$ (R = t-Bu, Ph; R^1 = Me, Et, Me_3Si; $n = 0.1$), which are potential cross-linking agents [30]. The method is based on cross metathesis of vinyl(trialkoxy)- and vinyltris(trimethylsiloxy)silanes with vinyl (or allyl) $tert$-butyl (or phenyl) sul-

fide, catalyzed by second-generation Grubbs catalyst, [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolyldiphenylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium.

The reaction of organylthiomagnesium halides $RSMgX$ (X = I, Br) with halomethyltriethoxysilane $XCH_2Si(OC_2H_5)_3$ (X = Cl, I) in ether and acetonitrile was studied with the aim of preparing trialkoxysilylmethyl-substituted sulfides [31].

For example, bis(triethoxysilylmethyl) sulfide $[(C_2H_5O)_3SiCH_2]_2S$, methyl triethoxysilylmethyl disulfide $CH_3SSCH_2Si(OC_2H_5)_3$, and 2,2,6,6-tetraethoxy-2,6-disila-4-thia-1-oxane were isolated from a complex mixture of products formed in the reaction of CH_3SMgI with $ICH_2Si(OC_2H_5)_3$. Refluxing of C_6H_5SMgBr with (chloromethyl)trimethoxysilane $ClCH_2Si(OCH)_3$ in THF yielded a mixture consisting mainly of phenyl trimethoxysilylmethyl sulfide and diphenyl disulfide.

A procedure for preparing organosilicon sulfides, similar in its essence to that described in [15–20], was suggested in [32]. In particular, the polysulfide $(EtO)_3Si(CH_2)_3S_x(CH_2)_3Si(OEt)_3$ (x = 2.36) was prepared by the reaction of 3-triethoxysilylpropyl chloride with a mixture obtained after heating sodium hydrosulfide with sodium hydroxide and sulfur at 140–150°C for 3 h under nitrogen and in anhydrous ethanol.

Patents [33, 34] concern synthesis of organosilicon sulfides and polysulfides of different compositions, recommended as cross-linking agents or additives for preparing high-quality vulcanized rubber for automobile tires. Such vulcanized rubbers are used as a base for producing automobile tires with well operation balance on ice roads, steering stability, and wear resistance [35].

A procedure was developed for preparing organosilicon sulfur-containing cross-linking agents containing sulfide and (or) thiol groups by the reaction of organosilicon acetals of type $R_x^1(R^2O)_{3-x}SiRCR^3(OR^2)_2$, where R is a saturated or unsaturated linear, branched, or cyclic bivalent hydrocarbon moiety with 2–12 carbon atoms, preferably containing bivalent –O– or –S– fragments; R^1 is an alkyl group with 1–4 carbon atoms; R^2 can be either an alkyl group like R^1 or a cyclic group; R^3 is a hydrogen atom or the same group as R^1, with sulfur-containing compounds of the general formula HSR^4, where R^4 is hydrogen, RSH, or $RSiR_x^1(OR^2)_{3-x}$ [36]. The reaction is performed in the presence of liq-

uid or solid Brønsted or Lewis acid catalysts taken in an amount of 0.05 to 5 wt %.

Patent [37] describes a rubber compound containing an organosilicon polysulfide $(C_nH_{2n+1}O)_3Si(CH_2)_mS_x(CH_2)_mSi(OH_{2n+1}C_n)_3$ (m = 1–5, n = 1–3, x ≥ 1). The compound is easily moldable and abrasion-resistant.
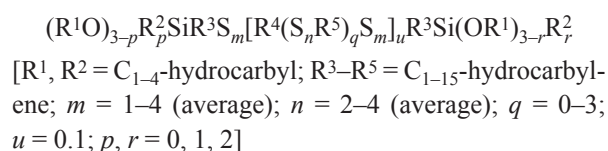
Sulfur-containing organosilicon compounds of the structure

I

II
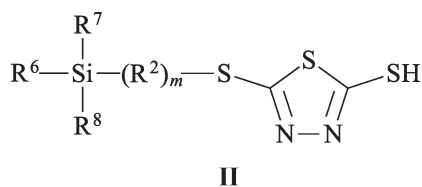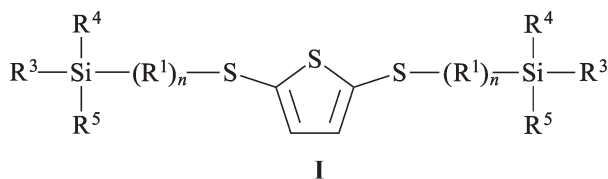
are suggested as cross-linking agents for preparing well-moldable, strong, and extensible compounds for rubber tires [38]. Compounds of this type are prepared, e.g., by the reaction of a mixture of 3-chloropropylchlorosilane with 1,3,4-thiadiazole-2,5-dithiol in 1 : 1 or 2 : 1 ratio at 100°C, performed for 24 h in the presence of methanol.

A rubber stock containing as one of the components bis(3-triethoxysilylpropyl) polysulfide in combination with glycidyloxypropyl(triethoxy)silane is suggested as a cross-linking agent for preparing molded items [39].

Rubber stocks containing organosilicon polysulfides of the general formula:

$$(R^1O)_{3-p}R_p^2SiR^3S_m[R^4(S_nR^5)_qS_m]_uR^3Si(OR^1)_{3-r}R_r^2$$
$[R^1, R^2 = C_{1-4}$-hydrocarbyl; $R^3–R^5 = C_{1-15}$-hydrocarbylene; m = 1–4 (average); n = 2–4 (average); q = 0–3; u = 0.1; p, r = 0, 1, 2]

in combination with SiO_2 were developed for producing automobile tires with decreased rolling resistance and enhanced wear resistance [40].

An interesting sorption material for taking up mercury vapor was developed on the basis of SiO_2 doped with copper and silanized with bis(3-triethoxysilylpropyl)-tetrasulfide [41]. The mercury absorption capacity of the sorption material containing 2.5% Cu and 6% S reaches 19.789 mg g^{-1}.

Trimethoxy-, trifluoro-, trihydro-, and hydro(phenyl)-chlorosilanes and hydro(phenyl)silyl triflate containing 2-(methylthiomethyl)phenyl substituent at the silicon atom were synthesized with the aim of preparing organosilicon compounds with possible intramolecular coordination of the sulfur atom with the silicon atom [42]. Weak coordination bond S→Si was found in trihydro- and hydro(phenyl)chloro-substituted compounds. However, only such S-donor compound as 2-MeSC$_6$H$_5$SiPh(H)(OTf) has a covalent structure with the five-coordinate silicon atom having trigonal-bipyramidal geometry:
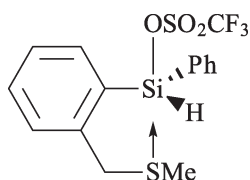
The similarly synthesized π-donor compound (Me)$_2$PC$_6$H$_5$SiPh(H)(OTf) has an ionic structure with the four-coordinate Si atom:
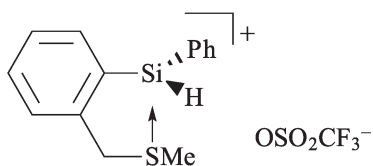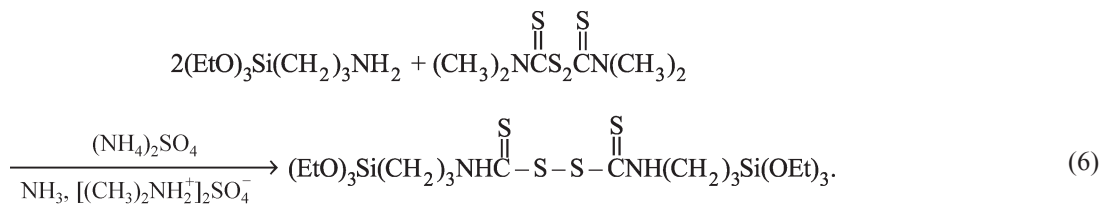
Organosilicon sulfides [(phenylthiomethyl)trimethyl- and (4-methylphenylthiomethyl)trimethylsilanes, and also bis(trimethylsilylmethylthiophenyl) sulfide] in combination with a xanthene dye (5,7-diiodo-3-butoxy-6-fluorene, DIBF) as sensitizer were studied as coinitiators of the photoinduced radical polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate [43].

Photochemical synthesis of very fine aerosol particles of organosilicon compounds from trimethyl(2-propynyloxy)silane and carbon disulfide has been performed [44]. The aerosol particles were prepared by irradiation of the gaseous mixture of the initial silane and CS$_2$ at 313 nm with a medium-pressure mercury lamp.
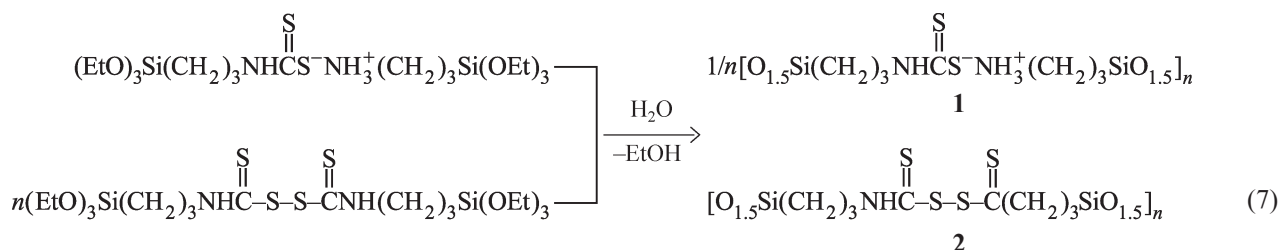
The development of the chemistry of organosilicon compounds with a carbofunctional sulfur-containing heteroatomic group is directly associated with such practically important field of organosilicon chemistry as organosilicon ion-exchange and complexing sorbents [45]. For example, data on the synthesis of N-(3-triethoxysilylpropyl)ammonium N-(3-triethoxysilylpropyl)dithiocarbamate, the product of the reaction of N-3-tri-ethoxysilylpropylamine (AGM-9) with carbon disulfide at 60°C, have been published relatively recently [46].

Bis-N,N'-(3-triethoxysilylpropyl)thiuram disulfide was prepared by condensation of AGM-9 with thiuram disulfide in the presence of a catalytic amount of ammonium sulfate [47]:

$$2(EtO)_3Si(CH_2)_3NH_2 + (CH_3)_2N\overset{\overset{S}{\|}}{C}S_2\overset{\overset{S}{\|}}{C}N(CH_3)_2$$

$$\xrightarrow[\text{NH}_3,\ [(CH_3)_2NH_2^+]_2SO_4^-]{(NH_4)_2SO_4} (EtO)_3Si(CH_2)_3NH\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}NH(CH_2)_3Si(OEt)_3. \tag{6}$$

Using the method of hydrolytic polycondensation of a mixture of N-(3-triethoxysilylpropyl)ammonium N-(3-triethoxysilylpropyl)dithiocarbamate [45] and bis-N,N'-(3-triethoxysilylpropyl)thiuram disulfide [46]

organosilicon cross-linked polymers of silsesquioxane structure, which contained dithiocarbamate (polymer **1**) and thiuram disulfide (polymer **2**) moieties, were produced:

$$(EtO)_3Si(CH_2)_3NH\overset{\overset{S}{\|}}{C}S^-NH_3^+(CH_2)_3Si(OEt)_3 \longrightarrow$$

$$\xrightarrow[-\text{EtOH}]{\text{H}_2\text{O}} 1/n[O_{1.5}Si(CH_2)_3NH\overset{\overset{S}{\|}}{C}S^-NH_3^+(CH_2)_3SiO_{1.5}]_n$$

1

$$n(EtO)_3Si(CH_2)_3NH\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}NH(CH_2)_3Si(OEt)_3 \longrightarrow [O_{1.5}Si(CH_2)_3NH\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}(CH_2)_3SiO_{1.5}]_n \tag{7}$$

2

Polymers **1** and **2** supplemented the series of ion-exchange and complexing sorbents [47]. A study of the activity of polymer I in sorption of such metals as silver, gold, platinum metals (platinum, palladium, rhodium), and mercury showed that the performance of the polymer as a sorbent of these metals from aqueous solutions decreased in the order Hg(II) > Ag(I) > Au(III) > Pd(II) > Pt(IV) > Rh(III). The ionic coordination mechanism of the metal sorption was suggested.

Polymer **2** studied as a sorbent of such elements as silver, gold, platinum, palladium, rhodium, arsenic, cadmium, cobalt, nickel, and copper showed very high performance in sorption of Ag(I), Hg(II), and especially Cu(II).
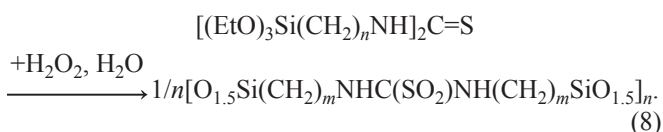
The sorption occurs by the coordination mechanism with the formation of an N,S-chelate:

$$
\begin{array}{ccccc}
Cu \!=\! S & & & S \!=\! Cu \\
| \; | & || & & || & | \; | \\
...HN & -C-S-S-C-HN
\end{array}
$$

$$[R_3Si(CH_2)_nNH]_2C{=}S + 2H_2O_2 \rightarrow [R_3Si(CH_2)_nNH]_2CSO_2 + H_2O, \qquad (9)$$
$$R = Me,\ Et;\ n = 1\text{–}3.$$
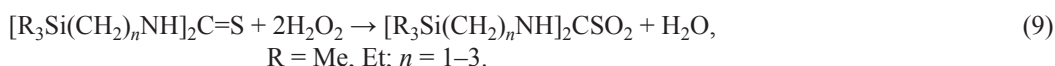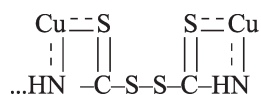
Oxidation of bis-*N,N'*-(3-silatranylpropyl)thiourea under the same conditions but in chloroform yielded

A zwitter-ionic structure was ascribed on the basis of the IR data to bis-*N,N'*-(trimethylsilylmethyl)- and bis-*N,N'*-(3-silatranylpropyl)-S,S-dioxothioureas and to organosilicon polymers containing the S,S-dioxothiourea moiety:

$$
\begin{array}{c}
R\!-\!HN \;\; +\;\; NH\!-\! \\
\quad\ \ C \\
\quad\ \ || \\
\quad\ \ S \\
O \diagup \!=\! \diagdown O
\end{array}
$$
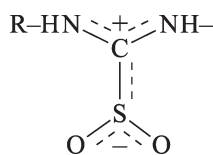
Bis-*N,N'*-(trialkylsilylalkyl)-*S,S*-dioxothioureas, like thiourea dioxide itself, exhibit reducing properties [55].
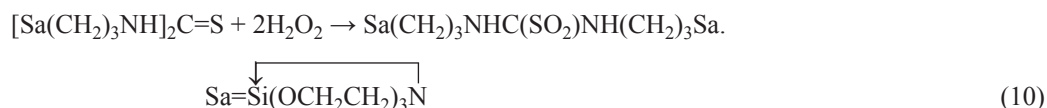
In addition, polymers **1** and **2**, like the starting monomers, exhibit metallochromic properties and are new potential test systems for the development of new test methods, which are now very demanded in analytical chemistry [48].

The first organosilicon polymers with metallochromic properties were poly [bis-*N,N'*-(silsesquioxanylalkyl)-S,S-dioxothioureas] [49]. They were synthesized by oxidative hydrolytic polycondensation of the corresponding bis-*N,N'*-(triethoxysilylalkyl)thioureas [50, 51]:

$$[(EtO)_3Si(CH_2)_nNH]_2C{=}S$$
$$\xrightarrow[\ \ \ \ \ \ \ \ \ ]{+H_2O_2,\ H_2O} 1/n[O_{1.5}Si(CH_2)_mNHC(SO_2)NH(CH_2)_mSiO_{1.5}]_n.$$
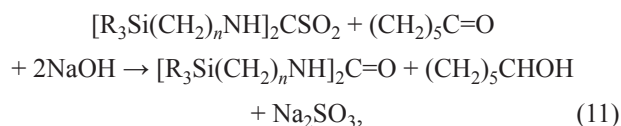$$(8)$$

Oxidation of bis-*N,N'*-(trialkylsilylalkyl)thioureas with 45–50% hydrogen peroxide at −5 to 0°C yielded the corresponding bis-*N,N'*-(trialkylsilylalkyl)-S,S-dioxothioureas [52, 53]:

bis-*N,N'*-(3-silatranylpropyl)-*S,S*-dioxothiourea [54]. In the process, the silatranyl group remains intact:

$$[Sa(CH_2)_3NH]_2C{=}S + 2H_2O_2 \rightarrow Sa(CH_2)_3NHC(SO_2)NH(CH_2)_3Sa.$$
$$Sa{=}Si(OCH_2CH_2)_3N \qquad (10)$$

Their reaction with cyclohexanone in aqueous-ethanol alkali solution yields cyclohexanol:

$$[R_3Si(CH_2)_nNH]_2CSO_2 + (CH_2)_5C{=}O$$
$$+\ 2NaOH \rightarrow [R_3Si(CH_2)_nNH]_2C{=}O + (CH_2)_5CHOH$$
$$+\ Na_2SO_3, \qquad (11)$$

where R = Me, Et; *n* = 1–3.

The reaction of poly[bis-*N,N'*-(silsesquioxanyl-propyl)-*S,S*-dioxothiourea] with ammonia and methylamine, yielding organosilicon polymers with the carbofunctional guanidine or methylguanidine group, is a rare process of substitution of one carbofunctional substitu-

ent by another one in the silsesquioxane matrix of the polymer without breakdown of its structure [56]. The reaction is exothermic and occurs within 10 min:

$$[O_{1.5}Si(CH_2)_3NH]_2CSO_2 + RNH_2$$
$$\rightarrow [O_{1.5}Si(CH_2)_3NH]_2C=HR + 2H^+ + SO_2^{2-}, \quad (12)$$
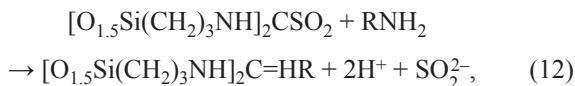
where R = H, Me.

Poly[bis-*N,N'*-(silsesquioxanylalkyl)-S,S-dioxothioureas] showed high performance in sorption of silver(I) and behaved as redox resins toward silver.

Poly[bis-*N,N'*-(silsesquioxanylpropyl)-S,S-dioxothiourea] was studied as sorbent for uranyl ions UO_2^{2+} [57]. The polymer showed the highest performance in uranyl sorption at pH 6.5. High distribution coefficient ($D = 7.3 \times 10^3$ cm^3 g^{-1}) shows that this polymer is promising for sorption recovery of microamounts of uranium(VI) from solutions.

In addition, poly[bis-*N,N'*-(silsesquioxanylpropyl)-S,S-dioxothiourea] showed high performance in sorption of vanadium(V) [58] and rare earth elements [59]. The polymer efficiently takes up vanadium at pH in the interval 2–9 in which the cationic vanadium species (VO_2^+) transforms into the anionic species (VO_3^-) [60]. The ampholytic properties of the polymer are due to the zwitter-ionic structure of its S,S-dioxothiourea substituent. The rare earth elements (the whole series from lanthanum to lutetium) are efficiently sorbed by the polymer at pH 5–6.

Both organosilicon polymers containing dithiocarbamate, thiuram disulfide, and *S,S*-dioxothiourea groups and the corresponding monomers exhibit metallochromic properties and are actually test systems of a new generation, promising for the development of efficient and rapid analytical test methods based on them [49].

High and peculiar sorption activity of organosilicon polymers containing the *S,S*-dioxothiourea group is quite consistent with the sorption properties of organosilicon polymeric thiourea derivatives themselves, in particu-

lar, of poly[bis-*N,N*-(silsesquioxanylpropyl)thiourea] (sorbents PSTM-3, PSTM-3T, or granulated PSTM-3S). A method based on chemical preconcentration and atomic emission for the determination of gold, platinum, and palladium in lean geological objects using PSTM-3 and PSTM-3T sorbents was developed and introduced into analytical practice [61].
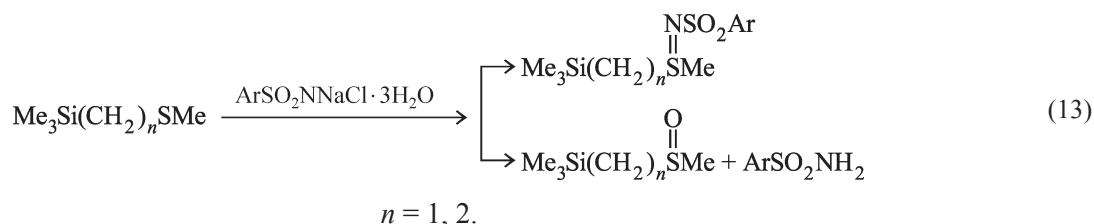
Sorbent PSTM-3S was used for developing a procedure for gold recovery from flotation concentrates [62]. The method consists in dissolution of the concentrates in a nitric acid thiourea solution, in which the concomitant elements Se, Te, V, Cr, and Ni do not dissolve, and subsequent sorption recovery of gold from a solution using PSTM-3S organosilicon sorbent. The degree of gold recovery with PSTM-3S is about 94.4%.

The organosilicon monomer containing a thiourea moiety, bis-*N,N*-(3-triethoxysilylpropyl)thiourea, was used for modification of Sibunit carbon sorbent [63]. The modified sorbent showed high activity in sorption of Pt(IV) ions from hydrochloric acid solutions.

Synthesis of an organosilicon compound containing a dithiourethane moiety is reported in a patent [64].

Synthesis and some properties of silyl sulfimides, potential complexing agents, have been described [65, 66]. The first acyclic organosilicon sulfimide containing the S=N group in the γ-position to the Si atom [67] was synthesized by the reaction of 3-trimethylsilylpropyl methyl sulfide with Chloramine-B in methanol.

However, similar synthesis of the compound with the sulfimide group in the α-position relative to the Si atom failed, because the starting trimethylsilylmethyl ethyl sulfide decomposed under these conditions with the release of the organic sulfimide. Voronkov et al. [68] were able to synthesize α- and β-silylsulfimides by the reaction of α- and β-silyl sulfides with *N*-chloroarenesulfonamides (Chloramine-B or -T) in the presence of benzyltriethylammonium chloride as phase-transfer catalyst in a CH$_2$Cl$_2$ solution at –5°C. However, the corresponding trimethylsilyl alkyl sulfoxides are also formed along with the desired α- and β-silyl sulfimides:

$$Me_3Si(CH_2)_nSMe \xrightarrow{ArSO_2NNaCl \cdot 3H_2O} \begin{cases} \overset{\displaystyle NSO_2Ar}{\underset{\parallel}{}} \\ Me_3Si(CH_2)_n\overset{\parallel}{S}Me \\[2ex] Me_3Si(CH_2)_n\overset{\displaystyle O}{\underset{\parallel}{S}}Me + ArSO_2NH_2 \end{cases} \quad (13)$$

$$n = 1, 2.$$

The first representatives of a new class of organosilicon compounds, 5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3]-undecanes, were synthesized in the early 1960s by ether interchange of four-coordinate silicon compounds of type $RSi(OR^1)_3$ with tris(2-hydroxyethyl)amine and its C-substituted derivatives. Voronkov suggested a brief name of these compounds, silatranes, which later came into common use [69].

Silatranes have a unique tricyclic structure in which the silicon and nitrogen atoms form a transannular coordination bond Si←N:
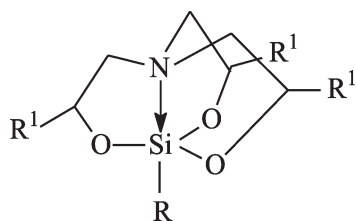
R, R^1 = H, Alkyl, organyl.

Extensive studies of this class of silicon compounds started after Voronkov et al. discovered in 1963 specific selective toxicity of 1-arylsilatranes: unusually high for warm-blooded animals (LD_{50} 0.1–0.5 mg kg^{-1}) and very low for ectotherms [70]. This fact disproved the opinion, commonly accepted previously, that organosilicon compounds are biologically inert. Recognition of the important role of silicon in living nature gave rise to a new science on the junction of chemistry, biology, and biochemistry: organosilicon biochemistry. Studies of diverse 1-oragnylsilatranes occupy a particular place in this science.

Since the 1970, Voronkov et al. initiated systematic studies in the field of biologically active carbofunctional 1-organylsilatranes $RSi(OCHR^1CH_2)_3N$, including 1-(mercaptoalkyl)silatranes and 1-(organylthioalkyl)silatranes of the $RS(CH_2)_m Si(OCH_2CH_2)_n(OCHMeCH_2)_{3-n}N$ general formula (R = H, alkyl, aralkyl, aryl, heteryl, etc.; m = 1–3; n = 0–3).

Particular attention was paid in the past two decades to the electronic structure and physicochemical properties of compounds of this type. For example, the first ionization potentials of the lone electron pair of the sulfur atom in compounds of the general formula $EtS(CH_2)_n SiX_3$, where SiX_3 = $Si(OMe)_3$, $Si(OEt)_3$, or $Si(OCHRCH_2)_3N$, R = H or Me, n = 1–3, were determined by He(I) photoelectron spectroscopy. The position of the charge-transfer bands in the electronic absorption spectra of complexes of these compounds with tetracyanoethylene was determined [71]. Linear correlations were found between the ionization potential of the lone electron pair of the sulfur atoms, frequency of the charge-transfer bands in complexes of these compounds with tetracyanoethylene, and basicity of these compounds, manifested in hydrogen bonding with phenol, on the one hand, and the inductive constants of the $(CH_2)_n SiX_3$ groups, on the other hand.

The data obtained show that all these groups are electron donors relative to the S atom at all values of n.

The deviations of the spectral characteristics of ethylthiomethyl(trialkoxy)silanes $EtSCH_2SiX_3$ (X = OMe, OEt) from the linear relationship are due to the n,σ^* interaction in the S–CH_2–Si fragment, manifested both in the gas phase and in the solution.

As a continuation of studies of sulfur-containing 1-alkylsilatranes in which the sulfur and silicon atoms form an S–CH_2–Si fragment, Brodskaya et al. [72] prepared previously unknown halides of S-(trimethoxysilylmethyl)isothiuronium, S-(silatranylmethyl)isothiuronium, and their N-substituted derivatives:

1–7
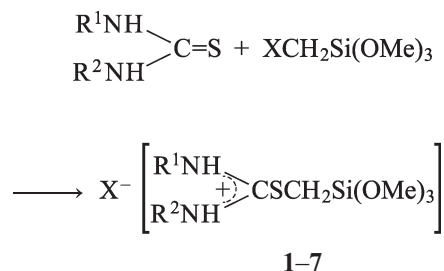
where $R^1 = R^2$ = H, X = Cl (**1**), I (**2**); $R^1 = R^2$ = Me, X = I (**3**); R^1 = H, R^2 = Ph, X = Br (**4**), I (**5**); $R^1 + R^2 = (CH_2)_2$; X = Cl (**6**), I (**7**).

$$\textbf{1–7} \ + \ (HOCH_2CH_2)_3N$$

8, **9**, **11**, **13–16**
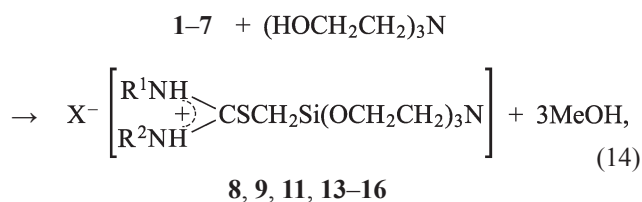
where $R^1 = R^2$ = H, X = Cl (**8**), I (**9**); $R^1 = R^2$ = Me, X = I (**11**); R^1 = H, R^2 = Ph, X = Br (**13**), I (**14**); $R^1 + R^2 = (CH_2)_2$; X = Cl (**15**), I (**16**).

The reaction was performed in methanol or chloroform and occurred relatively vigorously without any catalyst within 1–2 min.

Also, chlorides and iodides of *S*-(silatranylmethyl)-isothiuronium and of its N-substituted derivatives were prepared by the direct reaction of thiourea and its N-substituted derivatives with 1-halomethylsilatranes.

As shown by IR and UV spectroscopy, both *S*-(trimethoxysilylmethyl)isothiuronium and *S*-(silatranylmethyl)isothiuronium halides, as well as their N-substituted derivatives, exist in the solid state and in solutions (methanol, acetonitrile) in the form of two equilibrium salt structures with the positive charge on the nitrogen or carbon atom:

$$
\left[R\ SC \begin{array}{c} \overset{+}{N}H_2R^1 \\ \diagup \\ \diagdown \\ NR^2 \end{array} \right] X^- \rightleftarrows \left[R\ \overset{+}{SC} \begin{array}{c} NHR^1 \\ \diagup \\ \diagdown \\ NHR^2 \end{array} \right] X^- \quad (15)
$$

$$
\text{A} \qquad\qquad\qquad\qquad \text{B}
$$
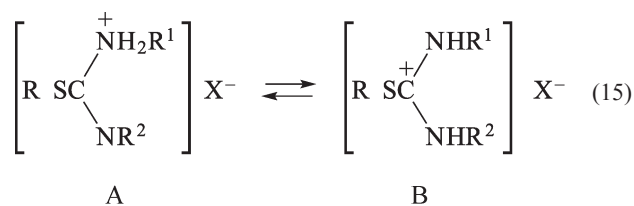
Proceeding with a search for biologically active silicon compounds, Brodskaya et al. [72] prepared 1,1-dimethylhydrazine derivatives, namely, 1,1-dimethylhydrazones of 3-(trimethoxysilylmethylthio)- and 3-(2-trimethoxysilylethylthio)butanals and of 3-silatranylmethyl(ethyl)thiobutanals.

Paper [72] summarizes the results of UV and IR studies of such potentially bioactive compounds as 8-quinolyl-, 2-benzothiazolyl-, and 2-benzoxazolylthiomethyl(trialkoxy)silatranes.

The chemistry of silatranes, which was initiated by Voronkov and then extensively developed by his disciples under his guidance, was also studied in other countries. This can be seen from one of recent reviews concerning the synthesis, structure, reactivity, and use of these compounds in medicine and agriculture [73].

There are patent data [74] on the preparation of silatranyl derivatives of alkyl sulfides and dialkyl sulfides, which are recommended as components of rubber stocks.

Kovăcs et al. [75] prepared and studied by NMR spectroscopy 1-(3-mercaptopropyl)-1,7,10-trimethylsilatrane. The compound was synthesized by ether interchange of 3-mercaptopropyl(trimethoxy)silane with tris(isopropanol)amine in xylene at 110°C in the presence of a catalytic amount of KOH.

3-Isothiocyanatopropylsilatrane was prepared by the reaction of 3-aminopropylsilatrane with dicyclohexylcarbodiimide and carbon disulfide, and its reaction with a series of Lewis acids and bases was studied [76]. The reactions with Lewis acids ($SnCl_4$, $TiCl_4$, $AgNO_3$) yield the corresponding complexes with the coordination via nitrogen or sulfur atoms of the thiocyanate group [scheme (16)]. The reaction of 3-isothiocyanatopropylsilatrane with diethylamine also yields a coordination compound [scheme (16)], as suggested, in the authors' opinion, by decreased intensity of the ν_{NH} absorption band in the IR spectrum of the adduct:

$$(16)$$
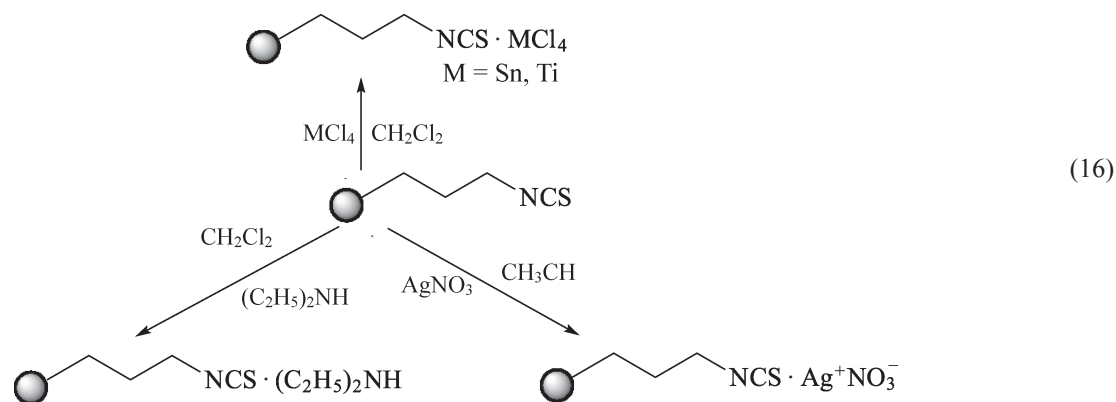
Quaternization of 3-aminopropylsilatrane with hydrogen chloride to obtain 3-(silatranyl)propylammonium chloride was studied [77]. In addition, 3-aminopropylsilatrane was involved in the nucleophilic addition to carbon disulfide in the presence of triethylamine, which led to the formation

of a new carbofunctional Si-substituted silatrane, triethylammonium 3-silatranylpropyldithiocarbamate. This compound was studied as bidentate ligand in reactions with Cu(II), Co(II), Ni(II), and Pd(II) salts. The Cu(II), Ni(II), and Pd(II) cations were found to form 1 : 2 complexes with triethylammonium-3-silatranylpropyldithiocarbamate (M : L), and the Co(II) cations, a 1 : 3 complex. The synthesized triethylammonium 3-silatranylpropyldithiocarbamate appeared to be active toward *Escherichia coli*, *Bacillus subtillus*, and *Staphylococcus aureus* bacteria.

There are patent data on the use of mercaptoalkyl-silatranes as modifying agents for the development of materials capable of fixation of metals on their surface [78]. The most widely used modifying agents are 3-mercaptopropylsilatrane and compounds of the general formula $RS(CH_2)_nSi(OCH_2CH_2)_3N$, where R is hydrogen, acetyl, *tert*-butoxycarbonyl, benzoyloxycarbonyl, methylthiomethyl, triphenylmethyl, or other group. The suggested substrates are polymethylsiloxanes, polycyclic olefins, cycloolefin polymers, poly(methyl methacrylate), polystyrene, polyethylene, polypropylene, polycarbonate, and polyvinyl chloride.

The organosilicon compound is immobilized on the substrate surface via condensation with surface hydroxy groups of the substrate:

(17)
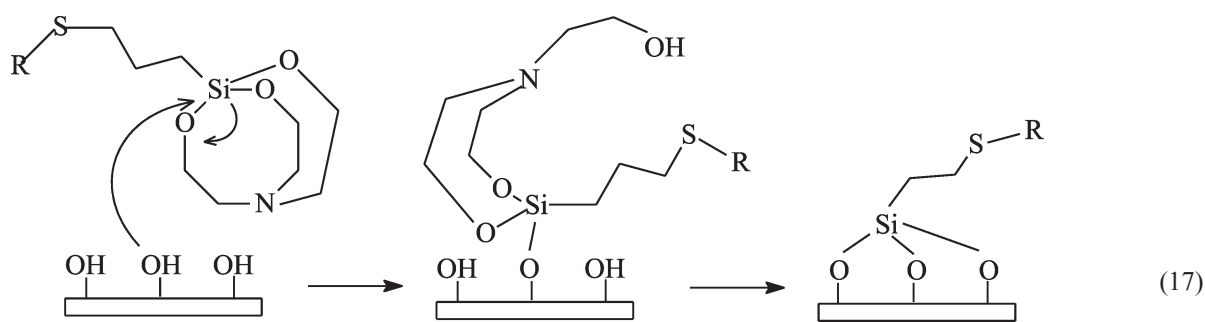
The metals being fixed are nanoparticles of gold, silver, platinum, palladium, or copper.

The suggested procedure for metal fixation can be used for modifying the surface of optical supports of different shapes, e.g., of optical sensor devices such as flat optical waveguide, cylindrical optical waveguide, tubular optical waveguide, optical gratings, etc. These devices are of much interest for the development of biomedical sensors of increased sensitivity, allowing more efficient detection of human diseases.

CONCLUSIONS

The data published in the past 15–20 years in the field of carbofunctional sulfur-containing organosilicon compounds convincingly prove their practical significance. This primarily concerns organosilicon sulfides and polysulfides, which are efficient cross-linking agents, additives for producing vulcanized rubbers for automobile tires and high-quality easily moldable and abrasion-resistant compounds, etc. [13, 20, 28, 29, 34, 37, 38]. The newly developed carbofunctional sulfur-containing organosilicon monomers and polymers [45, 46] made significant contribution to the progress of such field of organosilicon chemistry as chemistry of organosilicon ion-exchange and complexing sorbents [2] exhibiting metallochromic properties [49–51]. These substances are potential test systems of new generation. There has been also indubitable progress in the chemistry of 1-organylsilatranes with a sulfur-containing substituent at the silicon atom. Such compounds are potentially bioactive. In view of large practical potential of carbofunctional organosilicon compounds, further comprehensive studies in the field of carbofunctional sulfur-containing compounds are of doubtless interest.

REFERENCES

1. Voronkov, M.G. and Vlasova, N.N., in *Advances in Organosilicon Chemistry*, Moscow: Mir, 1985, p. 228.
2. Vlasova, N.N., Oborina, E.N., Grigor'eva, O.Yu., and Voronkov, M.G., *Russ. Chem. Rev.*, 2013, vol. 82, no. 5, pp. 449–464.
3. EP Patent 2149579 B1, Publ. 2011.
4. US Patent 20040210001 A, Publ. 2004.
5. Kaluderovic, G.N., Perez-Quintanilla, D., Zizak, Z., et al., *Dalton Trans.*, 2010, vol. 39, pp. 2597–2608.
6. US Patent 20060063879 A1, Publ. 2006.

7. CN Patent 102838981 A, Publ. 2012.

8. CN Patent 102977257 A, Publ. 2013.

9. CN Patent 103333199 B, Publ. 2013.

10. Chiu, S.J., Wang, S.Y., Chou, H.C., et al., *Langmuir,* 2014, vol. 30, no. 26, pp. 7676–7686.

11. DE Patent 19916498 A1, Publ. 2000.

12. JP Patent 2002220491 A, Publ. 2002.

13. EP Patent 0949263 A3, Publ. 2000.

14. US Patent 6194595 B1, Publ. 2001.

15. EP Patent 1247812 A1, Publ. 2002.

16. JP Patent 2002155091 A, Publ. 2002.

17. JP Patent 2002155093 A, Publ. 2002.

18. EP Patent 1279675 A2, Publ. 2003.

19. JP Patent 2005306784 A, Publ. 2005.

20. US Patent 20060106249 A1, Publ. 2006.

21. WO Patent 2004043969, Publ. 2004.

22. CN Patent 103073569 A 20130501, Publ. 2013.

23. US Patent 6448426 B1, Publ. 2002.

24. US Patent 6384256 B1 20020507, Publ. 2002.

25. US Patent 6384255 B1, Publ. 2002.

26. WO Patent 2003002573 A2, Publ. 2004.

27. CN Patent 102993228 A, Publ. 2013.

28. CN Patent 103342716 A, Publ. 2013.

29. JP Patent 2005298435 A, Publ. 2005.

30. Marciniec, B., Dariusz, K., and Krompiec, S., *J. Mol. Catal. A: Chemical,* 2004, vol. 224, nos. 1–2, pp. 111–116.

31. Sorokin, M.S. and Boronkov, M.G., *Russ. J. Gen. Chem.*, 2001, vol. 71, no. 12, pp. 1883–1890.

32. WO Patent 2009142222 A1, Publ. 2009.

33. JP Patent 2011236129 A, Publ. 2011.

34. JP Patent 2012106938 A, Publ. 2012.

35. JP Patent 2011252096 A, Publ. 2011.

36. US Patent 6518335 B2, Publ. 2003.

37. JP Patent 2013147532 A, Publ 2013.

38. KP Patent 2013044533, Publ. 2013.

39. WO Patent 2007085521 A1, Publ. 2007.

40. JP Patent 2008297357 A, Publ. 2008.

41. Mayer, D.E., Meeks, N., Sikdar, S., et al., *Energy Fuels*, 2008, vol. 22, no. 4, pp. 2290–2298.

42. Berlekamp, U.H., Mix, A., Neumann, B., et al., *J. Organomet.Chem.*, 2003, vol. 667, nos. 1–2, pp. 167–175.

43. Leniec, A., Jedrzejewska, B., and Paczkowski, J., *Polym. Bull.*, 2006, vol. 56, pp. 119–129.

44. Morita, H., Nozawa, R., Bastl, Zd., et al., *Photochem. Photobiol. A: Chemistry,* 2006, vol. 179, pp. 142–149.

45. Pozhidaev, Yu.N., Oborina, E.N., Belousova, L.I., et al., *Dokl. Chem.*, 2004, vol. 399, part 2, pp. 250–252.

46. Vlasova, N.N., Oborina, E.N., and Voronkov, M.G., *Dokl. Chem.*, 2011, vol. 439, part 1, pp. 190–193.

47. Voronkov, M.G., Vlasova, N.N., and Pozhidaev, Yu.N., *Appl. Organomet. Chem.*, 2000, vol. 14, pp. 287–313.

48. Zolotov, Yu.A., *Khimicheskie test-metody analiza* (Chemical Test Methods of Analysis), Moscow: URSS, 2002.

49. Vlasova, N.N., Oborina, E.N., Grigor'eva, O.Yu., and Voronkov, M.G., *Dokl. Chem.*, 2009, vol. 429, part 1, pp. 268–272.

50. Vlasova, N.N., Pozhidaev, Yu.N., Raspopina, O.Yu., et al., *Russ. J. Gen. Chem.*, 1999, vol. 69, no. 9, pp. 1391–1394.

51. Voronkov, M.G., Vlasova, N.N., Grigor'eva, O.Yu., et al., *Russ. J. Gen. Chem.*, 2005, vol. 75, no. 7, pp. 1091–1094.

52. Vlasova, N.N., Raspopina, O.Yu., Kashik, T.V., and Voronkov, M.G., *Russ. J. Gen. Chem.*, 2000, vol. 70. no. 10, p. 1651.

53. Vlasova, N.N., Grigor'eva, O.Yu., and Voronkov, M.G., *Russ. J. Gen. Chem.,* 2005, vol. 75, no. 6, pp. 860–862.

54. Vlasova, N.N., Grigor'eva, O.Yu., and Voronkov, M.G., *Russ. J. Gen. Chem.*, 2001, vol. 71, no. 12, p. 1950.

55. Vlasova, N.N., Raspopina, O.Yu., Pozhidaev, Yu.N., and Voronkov, M.G., *Russ. J. Gen. Chem.*, 2002, vol. 72, no. 1, pp. 55–58.

56. Vlasova, N.N., Grigor'eva, O.Yu., and Oborina, E.N., *Russ. J. Gen. Chem.*, 2006, vol. 76, no. 12, pp. 1870–1874.

57. Kirillov, A.I., Panezhda, E.V., Belousova, L.I., et al., *Russ. J. Appl. Chem.*, 2002, vol. 75, no. 5, pp. 724–727.

58. Pozhidaev, Yu.N., Panezhda, E.V., Grigor'eva, O.Yu., et al., *Dokl. Chem.*, 2003, vol. 389, nos. 4–6, pp. 97–100.

59. Pozhidaev, Yu.N., Panezhda, E.V., Grigor'eva, O.Yu., et al., *Dokl. Chem.*, 2003, vol. 393, no. 4–6, pp. 283–286.

60. Morachevskii, Yu.V. and Tserkovnitskaya, I.A., *Osnovy analiticheskoi khimii redkikh elementov* (Fundamentals of Analytical Chemistry of Rare Elements), Leningrad: Leningr. Gos. Univ., 1980.

61. Voronkov, M., Vlasova, N., Pozhidaev, Yu., et al., *Polym. Adv. Technol.,* 2006, vol. 17, no. 4, pp. 506–511.

62. Batnasan, A., Gunchin, B., Shirchinnamji, N., et al., *Int. J. Soc. Mater. Eng. Res.,* 2014, vol. 20, no. 1, pp. 29–34.

63. Pozhidaev, Yu.N., Lebedeva, O.V., and Sipkina, E.I., *Khim. Tekhnol.*, 2012, vol. 13, no. 11, pp. 670–675.

64. JP Patent 2012240922 A, Publ. 2012.

65. Kirpichenko, S.V., Suslova, E.N., Albanov, A.I., and Shainyan, B.A., *Sulfur. Lett.*, 2000, vol. 22, pp. 245–247.

66. Suslova, E.N., Kirpichenko, S.V., Albanov, A.I., and Shainyan, B.A., *J. Chem. Soc., Perkin Trans. I.*, 2000, no. 18, pp. 3140–3142.

67. Voronkov, M.G. and Zelchan, G.I., *Khim. Geterotsikl. Soedin.,* 1965, no. 1, pp. 51–57.

68. Voronkov, M.G., Zelchan, G.I., and Lukevics, E.J., *Kremnii i zhizn'* (Silicon and Life), Riga: Zinatne, 1978, 2nd ed.

69. Brodskaya, E.I., Sorokin, M.S., and Voronkov, M.G., *Russ. J. Gen. Chem.,* 2000, vol. 70, no. 7, pp. 1072–1076.

70. Sorokin, M.S., Lopyrev, V.A., Chipanina, N.N., et al., *Russ. J. Gen. Chem.*, 2004, vol. 74, no. 4, pp. 551–559.

71. Sorokin, M.S., Lopyrev, V.A., and Voronkov, M.G., *Russ. J. Gen. Chem.,* 2005, vol. 75, no. 6, pp. 891–901.

72. Brodskaya, E.I., Belyaeva, V.V., Trofimova, O.M., et al., *Russ. J. Gen. Chem.*, 2000, vol. 70, no. 7, pp. 1068–1072.

73. Puri, J.K., Singh, R., and Chahal, V.K., *Chem. Soc. Rev.*, 2011, vol. 40, no. 3, pp. 1791–1800.

74. DE Patent 10 2005 038791 AI, 2007.

75. Kovăcs, I., Matern, E., Sattler, E., et al., *J. Organomet.* Chem., 2009, vol. 694, pp. 14–20.

76. Singh, R., Puri, J.K., Chahal, V.K., Sharma, R.P., and Venugopalan, P., *J. Organomet. Chem.,* 2010, vol. 695, pp. 183–188.

77. Singh, R., Puri, J.K., Chahal, V.K., et al*., Synth. React. Inorg., Met.-Org. Nano-Met. Chem.*, 2012, vol. 42, no. 6, pp. 823–830.

78. US Patent 20140295075 A1, Publ. 2014.