*Russian Journal of General Chemistry, Vol. 75, No. 7, 2005, pp. 1091–1093. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 7, 2005, pp. 1154–1156.*
*Original Russian Text Copyright © 2005 by Voronkov, Vlasova, Grigor'eva, Pozhidaev, Bol'shakova.*

# *N*,*N*'-Bis(triethoxysilylmethyl)thiocarbamide and Poly[*N*,*N*'-bis(silsesquioxanylmethyl)thiocarbamide *S*,*S*-dioxide]

**M. G. Voronkov, N. N. Vlasova, O. Yu. Grigor'eva,**
**Yu. N. Pozhidaev, and S. A. Bol'shakova**

*Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia*

Received February 27, 2004

**Abstract**—Condensation of (aminomethyl)triethoxysilane with thiocarbamide in the presence of catalytic amounts of ammonium sulfate was used to synthesize *N*,*N*-bis(triethoxysilylmethyl)thiocarbamide. The latter was brought into oxidative hydrolytic polycondensation with $H_2O_2$ to obtain poly[*N*,*N*'-bis(silsesquioxanylmethyl)thiocarbamide *S*,*S*-dioxide] whose properties were compared with the properties of poly[*N*,*N*'-bis(silsesquioxanylpropyl)thiocarbamide *S*,*S*-dioxide]. Both polymers in highly acidic media rather strongly absorb Ag(I), while at pH 7 they reduce most absorbed $Ag^+$ to the metal. Their reaction with potassium permanganate involves reduction of $Mn^{7+}$ to $Mn^{4+}$. The first polymer is a less effective sorbent and redox agent than the second.

Previously we reported the synthesis of the first polysiloxane polymer containing a unique carbofunctional group $NHC(SO_2)NH$, viz. poly[*N*,*N*'-bis(silsesquioxanylpropyl)thiocarbamide *S*,*S*-dioxide] (**I**) [1]. This polymer was found to exhibit a number of unique properties. It effectively absorbs rare-earth metal ions with a fairly strong tetrad effect that is poorly understood in regard of rare-earth metals [2]. In reaction with rare-earth metal ions, such as vanadium(V), tungsten(VI), and molybdenum(VI), it functions as ampholite and reacts with both anionic and cationic forms of these metals [3]. Polymer **I**, like thiocarbamide dioxide and its organic derivatives [4], possesses redox properties [5].

Proceeding with the research into organosilicon polymers with ion-exchange and complexing properties, we have synthesized an analog of polymer **I** in which the silicon and nitrogen atoms are intervened by a methylene rather than trimethylene bridge, viz poly[*N*,*N*'-bis(silsesquioxanylmethyl)thiocarbamide *S*,*S*-dioxide] (**II**), and studied its properties. Polymer **II** was synthesized from previously unknown monomer *N*,*N*'-bis(triethoxysilylmethyl)thiocarbamide (**III**) was prepared by condensation of (aminomethyl)triethoxysilane (**IV**) with thiocarbamide in the presence of catalytic amounts of ammonium sulfate at 160–170°C [6, 7].

$$\underset{\textbf{IV}}{2(\mathrm{EtO})_3\mathrm{SiCH_2NH_2}} + \mathrm{H_2NC(S)NH_2}$$

$$\xrightarrow{(\mathrm{NH_4})_2\mathrm{SO_4}} \underset{\textbf{III}}{[(\mathrm{EtO})_3\mathrm{SiCH_2NH}]_2\mathrm{C{=}S}} + 2\mathrm{NH_3}.$$

Thiocarbamide **III** undergoes an extremely facile thermolysis into starting amine **IV** and triethoxysilylmethyl isothiocyanate (**V**).

$$\textbf{III} \xrightarrow{\Delta} \textbf{IV} + \underset{\textbf{V}}{(\mathrm{EtO})_3\mathrm{SiCH_2NCS}}.$$

We found that the optimal reaction temperature is 160–170°C. Since thiocarbamide **III** decomposed during vacuum distillation, its purification was performed by filtering the reaction mixture to remove solid admixtures and subsequent exposure to high vacuum (0.1–0.4 mm Hg) at room temperature. The lack in thiocarbamide **III** of an admixture of compound **V** was judged about by the disappearance from the IR spectrum of the characteristic N=C=S stretching absorption band at 2100–2000 $cm^{-1}$.

Polymer **II** was synthesized by oxidative hydrolytic polycondensation of thiocarbamide **III**. This method we developed previously [8] and used to prepare polymer **I** [1]. The synthesis involves concurrent and consecutive redox, hydrolysis, and polycondensation reactions of the starting organosilicon monomer under the action of 50–60% $H_2O_2$.

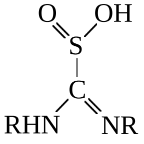
$$\textbf{III} \xrightarrow{\mathrm{H_2O_2,\ H_2O}} 1/n[(\mathrm{O_{1.5}SiCH_2NH_2CSO_2}]_n$$

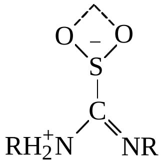
$$+ 6\mathrm{C_2H_5OH} + 3\mathrm{H_2O}.$$

The structure of polymer **II** is proved by its IR spectrum and chemical behavior. The IR spectrum contains a band at 1695 $cm^{-1}$ [ν(C=N)] that is also

1070-3632/05/7507-1091©2005 Pleiades Publishing, Inc.

present in the IR spectra of thiocarbamide dioxide [9], polymer **I** [1], and other known organosilicon derivatives of thiocarbamide dioxide [10, 11], which allows polymer **II** to be considered as a derivative of formamidinesulfinic acid **A** or zwitter ion **B**.


**A**


**B**

$R = CH_2SiO_{1.5}$.

Polymer **II** does not melt and dissolve or swell in water or organic solvents. It fairly actively absorbs Ag(I) and, like thiocarbamide dioxide [4] and organosilicon thiocarbamide *S,S*-dioxides [1, 5, 10], exhibits redox properties. Comparison of the sorption and redox activities of polymers **I** and **II** with respect to $Ag^+$ suggests that both polymers act as fairly effective sorbents for this metal in 1–3 M nitric acid. Therewith, polymer **I** is more active. The Ag(I) sorption capacity of these polymers depends on the acidity of the medium, and at pH 7 and in 0.1, 1, and 3 M $HNO_3$ it varies from 675 (pH 7) to 149 mg $g^{-1}$ (3 M $HNO_3$) for polymer **I** and from 624 (pH 7) to 107 mg $g^{-1}$ (3 M $HNO_3$) for polymer **II**.

In a weakly acidic medium (0.1 M $HNO_3$), both polymers commence to exhibit redox properties (5–10% $Ag^+$ is reduced to $Ag^0$). And, finally, in a neutral medium (pH 7) they behave primarily as redox agents and reduce ~80% of absorbed $Ag^+$ to $Ag^0$. However, with polymer **I** this process takes 10–20 min, while with polymer **II**, as long as 3–4 h.

$$2Ag^+ + 1/n\{[(O_{1.5}Si(CH_2)_mNH]_2CSO_2\}_n + 2H_2O$$

**I, II**

$$\longrightarrow 2Ag^0 + 1/n\{[O_{1.5}Si(CH_2)_mNH]_2C{=}O\}_n + H_2SO_3 + 2H^+.$$

In reaction with potassium permanganate polymer **II**, like polymer **I** [5], reduces $Mn^{7+}$ to $Mn^{4+}$.

$$3/n[(O_{1.5}SiCH_2NH)_2CSO_2]_n + 2KMnO_4 + 2H_2O$$
$$\longrightarrow 3/n[(O_{1.5}SiCH_2NH)_2C{=}O]_n + 2MnO_2$$
$$+ K_2SO_3 + 2H_2SO_3.$$

Polymer **I** is more reactive toward $Mn^{7+}$ than polymer **II**. The reductive capacity of polymer **I** is 1.67, 1.52, and 1.43 g $g^{-1}$ against 1.22, 1.52, and 1.08 g $g^{-1}$ for polymer **II** in 0.01 M $H_2SO_4$, at pH 7, and in 0.01 M $NH_4OH$, respectively.

The same effect we also observed in polyorganosiloxanes containing $Si(CH_2)_3Y$ and $SiCH_2Y$ (Y = $SO_3H$) groups [8]. This observation suggests that the $Si(CH_2)_nY$ group in the silsesquioxane skeleton is sterically more accessible at *n* = 3.

## EXPERIMENTAL

The IR spectra were measured on a UR-20 instrument in thin films. Spectrophotometry was performed on a KFK-2 photocolorimeter.

The starting (chloromethyl)triethoxysilane was prepared by the reaction of trichloro(chloromethyl)silane with absolute ethanol [12].

**(Aminomethyl)triethoxysilane (IV).** (Chloromethyl)triethoxysilane, 42.5 g, and 100 ml of liquid ammonia dried with metallic sodium and passed through a NaOH bed were placed in a 1-l autoclave. The autoclave was heated for 6 h at 125°C; therewith, the pressure in the autoclave rose to reach 115 atm. The ammonia was then removed, and the product was extracted from the residue with ether and isolated by vacuum distillation. Yield 7.8 g (20%), bp 53–55°C (3 mm Hg), $n_D^{25}$ 1.4090 {published data [12]: bp 80.5°C (14 mm Hg), $n_D^{25}$ 1.4082}. In addition, 5.0 g (12%) of *N,N*-bis(triethoxysilylmethyl)amine was isolated, bp 130°C (3 mm Hg), $n_D^{23}$ 1.4180 {published data [13]: bp 117°C (3 mm Hg), $n_D^{25}$ 1.4132}.

***N,N*'-Bis(triethoxysilylmethyl)thiocarbamide (III).** A mixture of 3 g of (aminomethyl)triethoxysilane (**IV**), 0.59 g of thiocarbamide, and 0.01 g of ammonium sulfate was heated in a sealed ampule at 160–170°C for 7 h. Thiocarbamide **II**, 3.9 g (60%), was isolated, $n_D^{20}$ 1.4240. IR spectrum, $cm^{-1}$: 3300 [ν(NH)], 2980 and 2880 [ν(CH)], 1520 [δ(NH)], 1440 [ν(CH)], 1260 [ν(CN)], 1140 [ν(C=S)], 1090–1050 [ν(SiOEt)]. Found, %: C 43.32; H 8.14; S 7.02; Si 11.60. $C_{15}H_{36}N_2O_6SSi_2$. Calculated, %: C 42.06; H 8.40; S 7.47; Si 13.08.

**Poly[*N,N*'-bis(silsesquioxanylmethyl)thiocarbamide *S,S*-dioxide] (II).** To a solution of 2.2 g of thiocarbamide **II** in 10 ml of chloroform, 0.34 g of 60% $H_2O_2$ was added dropwise with cooling to –5 to 0°C. The mixture was stirred at room temperature for 2 h. Yield 1 g (50%). IR spectrum, $cm^{-1}$: 1695 [ν(C=N)], 1400 [δ(CH)], 1260 [ν(CN)], 1100 [ν(SiOSi)], 1010 [ν(SO)], 620 [ν(CS)]. Found, %: C 16.56; N 11.73; S 11.79. $C_3H_7N_2Si_2S_1$. Calculated, %: C 15.12; N 11.76; S 13.44.

**Sorption of Ag(I) with polymers I and II.** Polymer **I** or **II**, 0.05 g, was stirred for 2 h at room temperature with 50 ml of a solution of $AgNO_3$, containing 0.01–0.2 mg $ml^{-1}$ $Ag^+$. The acidity of the medium was varied from neutral (pH 7) to strongly acidic (3.0 M $HNO_3$). After the process had been complete, the polymer was filtered off, and the filtrate was analyzed for $Ag^+$ by spectrophotometry with Dithizone [14], and the analysis results were used to estimate the recovery of Ag(I) and statistical sorption capacity.

**Reaction of polymers I and II with potassium permanganate.** Solutions of $KMnO_4$ in neutral (pH 7), acidic (0.05 M $H_2SO_4$), and alkaline (0.05 M $NH_4OH$) media were studied. A solution, 50 ml, containing 10 mg of Mn(VII) was sirred at room temperature for 2 h with 0.1 g of polymer **I** or **II**. A dark brown precipitate formed and was filtered off, dried in a vacuum dessicator, and weighed. The weight of $MnO_2$ was determined by the weight of the precipitate minum the weight of the polymer.

## ACKNOWLEDGMENTS

The work was financially supported by the *Leading Scientific Schools* Program (grant no. NSh-1129-2003.3).

## REFERENCES

1. Vlasova, N.N., Pozhidaev, Yu.N., Raspopina, O.Yu., Belousova, L.I., and Voronkov, M.G., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 9, p. 1446.
2. Pozhidaev, Yu.N., Panezhda, E.V., Grigor'eva, O.Yu., Kirillov, A.I., Belousova, L.I., Vlasova, N.N., and Voronkov, M.G., *Dokl. Ross. Akad. Nauk*, 2003, vol. 393, no. 5, p. 629.
3. Pozhidaev, Yu.N., Panezhda, E.V., Grigor'eva, O.Yu., Kirillov, A.I., Belousova, L.I., Vlasova, N.N., and Voronkov, M.G., *Dokl. Ross. Akad. Nauk*, 2003, vol. 389, no. 6, p. 768.
4. Budanov, V.V. and Makarov, S.V., *Khimiya serosoderzhashchikh vosstanovitelei* (Chemistry of Sulfur-containing Reducers), Moscow: Khimiya, 1994.
5. Vlasova, N.N., Raspopina, O.Yu., Pozhidaev, Yu.N., and Voronkov, M.G., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 1, p. 61.
6. Vlasova, N.N., Pestunovich, A.E., and Voronkov, M.G., *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1982, no. 10, p. 2380.
7. Voronkov, M.G., Pestunovich, A.E., Sterenberg, B.Z., Pusechkina, T.A., and Vlasova, N.N., *Z. Chem.*, 1983, vol. 23, no. 7, p. 248.
8. Vlasova, N.N., Stanevich, L.M., Kirillov, A.I., and Voronkov, M.G., *Izv. Sib. Otd. Akad. Nauk SSSR*, *Ser. Khim. Khim. Nauk*, 1987, issue 1. no. 2, p. 107.
9. Kharitonov, Yu.Ya. and Prokof'eva, I.V., *Dokl. Akad. Nauk SSSR*, 1965, vol. 162, no. 4, p. 829.
10. Vlasova, N.N., Raspopina, O.Yu., Kashik, T.V., and Voronkov, M.G., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 10, p. 1754.
11. Vlasova, N.N., Grigor'eva, O.Yu., and Voronkov, M.G., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 12, p. 2057.
12. Fialova, V., Bazant, V., and Chvolovsky, V., *Collect. Czech. Chem. Commun.*, 1973, vol. 38, no. 12, p. 3837.
13. Noll, J., Speier, J., and Daubert, B., *J. Am. Chem. Soc.*, 1951, vol. 73, no. 8, p. 3867.
14. Marczenko, Z., *Kolorymetryczne oznaczanie pierwiastków* (Colorimetric Determination of Elements), Warsaw: Wydawnictwa Naukowo-Techiczne, 1968. Translated under the title *Fotometricheskoe opredelenie elementov*, Moscow: Mir, 1971, p. 361.