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Complexation of Poly-bis-(3-silsesquioxanylpropyl)amino-sulfoxide and -sulfone with Rare-Earth Elements

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ABSTRACT

Polymers of silsesquioxane structure, poly[bis-(3-silsesquioxanyl-propylamino)]sulfoxide (**IV**) *and -sulfone* (**V**) *have been prepared and examined as complexation agents toward samarium(III) and thulium(III). Polymer* **IV** *was an effective complexation agent toward both of these elements. However, polymer* **V** *was an effective complexation agent only toward thulium(III) ions.*

The selective complexation of polymer **V** *with thulium is not affected by the presence of excess amounts of lanthanum, cerium, neodymium, or samarium salt. This suggests that polymer* **V** *may prove to be useful in rare-earth element (REE) separation and isolation. The selective complexation of* **V** *with thulium(III) is also observed in the presence of nickel(II), copper(II), or lead(II) salt.*

In developing the synthesis of new carbofunctional organosilicon monomers and polymers containing complex-forming and iogenic groups [1,2], we have studied the reaction of 3-triethoxysilylpropylamine (**I**) with sulfuryl chloride and thionyl chloride. The condensation of organosilicon amine (**I**) with SO_2Cl_2 and $SOCl_2$ was carried out at 0–(+5°C) in the presence of pyridine as an HCl acceptor for 24 hours to give organosilicon monomers **II** and **III** in nearly quantitative yield. However, owing to thermal decomposition, it was not possible to isolate these monomers by distillation in a high vacuum.

$$2(EtO)_3Si(CH_2)_3NH_2 + Cl_2SO_n + 2C_5H_5N$$
$$\rightarrow [(EtO)_3Si(CH_2)_3NH]_2SO_n + 2C_5H_5N \cdot HCl$$
$$n = 1\ (\mathbf{II}),\quad n = 2\ (\mathbf{III})$$

Under the action of 6M aqueous ammonia, monomers **II** and **III** were readily converted by hydrolytic condensation to the corresponding polymers of silsesquioxane structure, poly[bis-(3-silsesquioxanylpropylamino)]sulfoxide (**IV**) and -sulfone (**V**).

$$n[(EtO)_3Si(CH_2)_3NH]_2SO_n + 6_nH_2O$$
$$\rightarrow [(O_{o/5}Si(CH_2)_3NH)_2SO_n]_n + 6_nEtOH$$
$$n = 1\ (\mathbf{IV}),\quad n = 2\ (\mathbf{V})$$

The cross-linked structure of these polymers is attested to by their infusibility, nonswelling, and insolubility in water and organic solvents.

Polymers **IV** and **V** are yellow powders, the composition and structures of which were proved by IR spectroscopy. IR spectra show the absorption bands of the Si–O–Si group at 1100–1050 cm^{-1}, the NH group at 3320 cm^{-1}, the SO group at 1060 cm^{-1}, the NH group at 3250 cm^{-1}, and the SO_2 group at 1300–1130 cm^{-1}. The data of elemental analyses are presented in Table 1.

Due to the presence of the $NHSO_nNH$ group (n = 1, 2), the carbofunctional polysiloxanes **IV** and **V** are of great interest as potential complexation agents [3].

We have examined the complexation ability of

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TABLE 1 Elemental Composition of Polymers **IV** and **V**

	C	*H*	*Si*	*S*	*N*
		Polymer **IV**			
Found	27.75	5.90	20.51	10.93	5.83
Calculated	27.06	5.26	21.05	12.03	6.86
		Polymer **V**			
Found	25.51	5.35	19.43	9.08	8.93
Calculated	25.53	4.96	19.85	11.34	9.92

polymers **IV** and **V** relative to rare-earth elements (REE) with samarium(III) and thulium(III) which are members of the cerium and yttrium subgroups, respectively. Polymer **IV** turned out to be an effective complexation agent with respect to the two elements. Optimal complexation was provided at pH = 6 (Table 2). The contact times with aqueous samarium(III) and thulium(III) solutions are 0.5 and 2 hours, respectively (Table 3). Polymer **IV** is more prone to complex with samarium(III) than with thulium(III). This is evidenced by a faster establishment of equilibrium and a considerably greater amount of complexed metal. The static optical sorption capacities of the complexing reagent **IV** with respect to samarium(III) and thulium(III) are 212 and 175 mg/g, respectively.

TABLE 2 Dependence of REE Ion Sorption from Solutions at Various Acidities

Polymer **IV**				Polymer *V*	
pH	*Extraction of Sm(III) Ions (%)*	*pH*	*Extraction of Tm(III) Ions (%)*	pH	Extraction of Tm(*III*) Ions (%)
0.5	15.0	0.5	2.5	0.5	67.5
2.3	50.0	2.7	20.0	2.5	77.5
4.2	87.5	3.3	35.0	4.1	80.0
5.5	92.5	5.0	50.0	5.2	80.0
6.0	95.0	6.0	69.5	6.0	80.0
7.5	95.5	7.1	72.5	7.0	80.0
		8.2	72.5	8.0	69.0

TABLE 3 Dependence on Time of REE Ions Extraction from Solution

	Polymer **IV**		*Polymer* **V**
Time (Min)	*Extraction of Sm(III) Ions (%)*	*Extraction of Tm(III) Ions (%)*	*Extraction of TM(III) Ions (%)*
5	26	15	71
15	45	53.7	74
30	96	69.7	80
60	96	72.5	80
90	96	72.5	80

TABLE 4 Dependence of the REE Extraction Degree on Ionic Radii

Element	*Ionic Radius (Å) [4]*	*Degree of Extraction (%)*
Europium	0.950	3.5
Gadolinium	0.938	3.5
Terbium	0.923	7.2
Dysprosium	0.908	9.0
Holmium	0.894	15.0
Erbium	0.881	72.0
Thulium	0.869	80.0
Ytterbium	0.858	79.0
Lutetium	0.848	75.0

The complexing reagent **IV** is selective toward elements of the lanthanoid group even in a background of prevailing non-REEs such as nickel(II), copper(II), and lead(II). Unlike **IV**, the complexing reagent **V** is efficiently complexed only to thulium(III) ions. Complexation of **V** to samarium(III) has not been observed. The highest complexation of **V** to thulium is at a pH of 4–7 (Table 4), the contact time being 30 minutes. The static sorption capacity with respect to thulium(III) is 130 mg/g. The degree of REE extraction from solutions by the use of **V** indicates this complexing reagent to be highly efficient toward elements of the lanthanoid series (Table 4).

The selective complexation of polymer **V** with thulium is not affected by the presence of a 50-fold excess of lanthanum, a 20-fold excess of cerium, a 5-fold excess of neodymium, or a 2-fold excess of samarium. This opens up new promising ways for the application of complexing reagent **V** for REE separation and isolation. The selectivity of complexation of **V** with thulium(III) is also observed in the presence of such elements as nickel(II), copper(II), and lead(II).

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