

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

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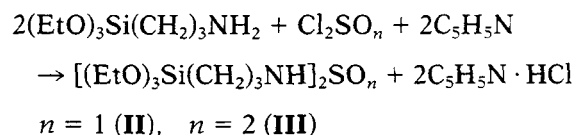
ABSTRACT

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.

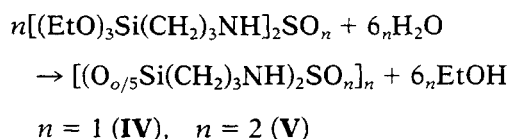
The selective complexation of polymer **V** with thulium is not affected by the presence of excess amounts of lanthanum, cerium, neodymium, or samarium salt. This suggests that polymer **V** may prove to be useful in rare-earth element (REE) separation and isolation. The selective complexation of **V**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



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**).



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

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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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

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

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

TABLE 3 Dependence on Time of REE Ions Extraction from Solution

Time (Min)	Polymer IV		Polymer V
	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

with respect to samarium(III) and thulium(III) are 212 and 175 mg/g, respectively.

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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