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Synthesis of Polymolybdenophenylsiloxane

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Abstract—Polymolybdenophenylsiloxane containing Mo(V) atoms and preserving the Si : Mo ratio equal to that in the starting mixture was prepared by the reaction of molybdenum(V) oxychloride dimethyl sulfoxide crystal solvate with sodium polyphenylsiliconate in the presence of dimethyl sulfoxide. The influence of the reaction conditions on the nature and yields of products was examined. Experiments on thermal oxidative degradation of polymolybdenophenylsiloxane showed that it is more stable compared to the previously studied polymetalloorganosiloxanes containing various *d* elements with the stoichiometric Si : metal ratio.

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The simplest and versatile process for the formation of heterosiloxane fragments in synthesis of metal-containing organosilicon compounds is the reaction of metal chlorides with alkali metal organylsilanolates [1]. To prepare polymetallophenylsiloxanes, it is appropriate to use a procedure with dimethyl sulfoxide (DMSO) as one of the solvents. In this case, the yields of the target products are virtually quantitative, and the polymers obtained are uniform in the composition and structure [2].

It was found previously that polyheterosiloxanes containing *d* elements have high heat resistance and act as effective thermostabilizers of polydimethylsiloxane rubber (SKTN) and as catalysts of some organic reactions [1].

Data on polyheterosiloxanes containing metals in oxidation states 5 and higher are extremely scarce [1]. From this viewpoint, molybdenum-containing polymers are of doubtless interest. The most accessible among molybdenum halides is molybdenum pentachloride which reacts with DMSO to form the compound $MoOCl_3 \cdot 2DMSO$ [3]. Polymolybdenophenylsiloxane (PMoPS) was prepared by the following schemes:

$$(PhSiO_{1.5})_n + n NaOH \rightarrow [PhSi(O)ONa]_n + nH_2O$$

$$n MoOCl_3 \cdot 2DMSO + 3[PhSi(O)ONa]_n \rightarrow [(PhSiO_{1.5})_3MoO_{2.5}]_n + 3n NaCl + 2n DMSO.$$

Polymolybdenophenylsiloxane sample PMoPS-1 was prepared by the reaction of the complex $MoCl_3 \cdot 2DMSO$ with sodium polyphenylsiliconate in the toluene–DMSO system. The synthesis was performed at 60°C in a heterogeneous system ($MoOCl_3 \cdot 2DMSO$ is insoluble in toluene). Under milder conditions, the components do not react with each other. The polymer was isolated from the solution in DMSO by precipitation with water. The analytical data, fractionation results (fractional precipitation), and yield of PMoPS-1 are given in the table.

The yield of the polymer fraction soluble in organic solvents was low, although the amount of the precipitated NaCl corresponded to the reaction stoichiometry. From the aqueous filtrate obtained in the course of product isolation, we recovered water-soluble products which, according to elemental analysis (see table), contained the main amount of molybdenum. The Si/M ratio in the polymer differed from the initial ratio, which can be attributed to the fact that the synthesis was performed under heterogeneous conditions at elevated temperatures. Under these conditions, DMSO ceases to exert a protective effect, and in the presence of even minor amounts of water the hydrolytic processes play the major role in formation of the polymer structure:

$$>Mo(O)–Cl + H_2O \rightarrow >Mo(O)–OH + HCl, \quad (1)$$

$$\equiv Si–ONa + HCl \rightarrow \equiv Si–OH + NaCl, \quad (2)$$

$$>Mo(O)–OH + HO–(O)Mo< \rightarrow >Mo(O)–O–(O)Mo< + H_2O, \quad (3)$$

Results of elemental analysis of the compounds obtained

Polymer index	Unit formula	Initial Si/Mo ratio	Si/Mo ratio in product	Yield, %	Found, %			Calculated, %		
					Mo	Si	C	Mo	Si	C
PMoPS--1	$(PhSiO_{1.5})_{10.8}MoO_{2.5}$	3	10.8	54.4	6.1	19.9	51.2	6.3	19.3	50.9
Fraction 1	$(PhSiO_{1.5})_{8.2}MoO_{2.5}$		8.2	40.8	8.0	19.1		8.0	19.2	
Fraction 2	$(PhSiO_{1.5})_{13.5}MoO_{2.5}$		13.5	58.6	5.1	20.1		5.1	21.1	
Water-soluble products	$(PhSiO_{1.5})_{1.1}MoO_{2.5}$		1.1	44.0	34.2	11.3		34.5	11.1	
PMoPS--2	$(PhSiO_{1.5})_{4.2}MoO_{2.5}$	3	4.2	60.2	14.0	17.4	44.9	14.1	17.3	44.6
Fraction 1	$(PhSiO_{1.5})_{2.8}MoO_{2.5}$		2.8	45.3	19.2	15.6		19.3	15.8	
Fraction 2	$(PhSiO_{1.5})_{5.9}MoO_{2.5}$		5.9	53.9	10.7	18.3		10.7	18.4	
Water-soluble products	$(PhSiO_{1.5})_{1.9}MoO_{2.5}$		1.9	39.4	25.2	14.0		25.2	14.0	
PMoPS--3	$(PhSiO_{1.5})_3MoO_{2.5}$	3	3.0	99.1	18.2	16.0	41.7	18.4	16.1	41.3
Fraction 1	$(PhSiO_{1.5})_{2.6}MoO_{2.5}$		2.6	53.8	20.3	15.4		20.4	15.5	
Fraction 2	$(PhSiO_{1.5})_{3.7}MoO_{2.5}$		3.7	45.1	15.8	17.1		15.7	16.9	

$$\equiv Si–OH + HO–Si\equiv \rightarrow \equiv Si–O–Si\equiv + H_2O, \quad (4)$$

$$>Mo(O)–OH + HO–Si\equiv \rightarrow >Mo(O)–O–Si\equiv + H_2O. \quad (5)$$

An attempt to perform the synthesis at room temperature in DMSO (with the aim of homogenization of the system; sample PMoPS-2) also failed to give a positive result. In this case, NaCl was not formed at room temperature, and therefore the temperature was elevated to 60°C. The weight of the NaCl precipitate corresponded to the reaction stoichiometry. The reaction products were isolated from the solution similarly to the synthesis of PMoPS-1. The results are given in the table. The yield of the polymer soluble in organic solvents somewhat increased, the Si/Mo ratio in it was closer to the initial ratio, but again molybdenum-rich water-soluble products were formed.

We believe that this ambiguous synthesis pattern is due to the fact that polymeric products contain >Mo(O)–OH fragments. This group is apparently acidic [3]. The presence of hydroxy groups at the Mo atoms in water-soluble compounds is also confirmed by the fact that these solutions are strongly acidic (pH 1). These groups are responsible for the solubility of such products in water. It is known that metallosiloxane groups are readily cleaved by protons, which can favor complete extraction of a metal from a polyheterosiloxane [4]. The presence of such groups in the polymer may induce formation of water-soluble Mo compounds in the step of polymer isolation [5], but immediately after isolation from solution these compounds lose the solubility both in water and in organic solvents.

In the synthesis of sample PMoPS-3, we changed the procedue for isolation of the final product and excluded its interaction with water. To a polymer solution prepared under the conditions similar to the synthesis of PMoPS-1, after separating the NaCl precipitate we added excess $CaCl_2$, which bound the DMSO occurring in the system. Toluene was distilled off, and the polymer was dried to constant weight. The results of the synthesis are given in the table.

As can be seen, PMoPS-3 is obtained in a quantitative yield, with the Si/M ratio equal to the initial ratio. The polymer does not form water-soluble compounds even on refluxing in the water–isopropanol system. Thus, it can be concluded that water-soluble products are formed specifically in the course of polymer isolation. The absence of water-soluble Mo-containing compounds in the synthesis of PMoPS-3 can be attributed to the fact that in this case the heterosiloxane fragments are finally formed in the step of isolation and drying of the polymer by homo- and heterocon-

densation of hydroxyl-containing products [Eqs. (3)–(5)].

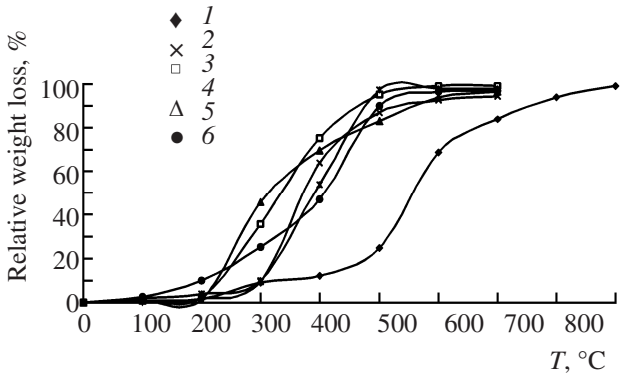
The above-described results are well consistent with the interaction schemes. With a decrease in the temperature, the yield of products soluble in organic solvents increases, the Mo content approaches the theoretical level, and the polymers become more uniform in the composition. The yield of PMoPS-3 is virtually quantitative, the Si/Mo ratio is equal to the initial value, and only certain nonuniformity in the composition is observed.

The IR spectra of all the PMoPS samples are similar, showing an absorption maximum at about 1050 cm^{-1} whose relative intensity grows with an increase in the Mo content of the polymer. Therefore, this maximum can be assigned to asymmetric vibrations of the Si–O–(M=O) bond. In this range there are no clearly pronounced maxima assignable to cyclic siloxane fragments, and only the band at 1136 cm^{-1} is considerably broadened. We believe that such a pattern in the range of absorption of siloxane bonds is indicative of an irregular structure of the polymer, without prevalence of cyclic fragments of any type.

The PMoPS samples are light brown solids readily soluble in the majority of organic solvents and insoluble in saturated hydrocarbons. They decompose without melting. According to gel permeation chromatography, PMoPS samples have the molecular weight higher than 5000 and do not contain low-molecular-weight impurities.

Thus, polymolybdophenylsiloxane preserving the Si/Mo ratio equal to the initial value can be prepared by the reaction of $MoOCl_3 \cdot 2DMSO$ with sodium polyphenylsiliconate in the presence of DMSO, if the interaction of the product with water in the step of isolation is excluded. The nature of the synthesis products is strongly affected by processes caused by hydrolysis of the starting compounds. These processes cannot be fully excluded because of the low reactivity of the crystal solvate $MoOCl_3 \cdot 2DMSO$.

Experiments on thermal oxidative degradation of PMoPS-3 showed that it is more stable than the previously studied polymetalloorganosiloxanes [6] containing various *d* elements with a stoichiometric Si : metal ratio (see figure). Intense thermal oxidation of PMoPS-3 starts at temperatures above 400°C and is complete at 900°C.



Thermograms of polymetallophenylsiloxanes containing *d* elements: (*1*) PMoPS (1 : 3), (*2*) PFePS (1 : 3), (*3*) PCoPS (1 : 3), (*4*) PCrPS (1 : 3), (*5*) PCuPS (1 : 2), and (*6*) PTiPS (1 : 4).

EXPERIMENTAL

Synthesis of polymolybdenophenylsiloxane, sample PMoPS-1. A solution of sodium polyphenylsiliconate prepared by the reaction of 3.13 g of polyphenylsilsesquioxane and 0.97 g of NaOH in 6 ml of DMSO and 31.4 ml of toluene was added to a solution of $MoOCl_3 \cdot 2DMSO$ prepared by the reaction of 2.24 g of $MoCl_5$ with 1.7 ml of DMSO. The reaction was performed at 60°C for 10 h. The NaCl precipitate was separated by centrifugation. The NaCl weight was 1.42 g (99% of theoretical amount). Toluene was distilled off, and the polymer was isolated from the DMSO solution by precipitation with a fourfold excess of water. The precipitate was dried at 100°C/20 mm Hg. Yield of the polymer 2.30 g (54.4%). The water-soluble products were isolated from the bright green filtrate by distillation of water and DMSO. The precipitate weight after drying at 120°C/5 mm Hg was 1.86 g (44.0% of theoretical yield).

Synthesis of polymolybdenophenylsiloxane, sample PMoPS-2. A solution of sodium polyphenylsiliconate prepared by the reaction of 7.74 g of polyphenylsilsesquioxane and 2.4 g of NaOH in 38.7 ml of DMSO and 38.7 ml of toluene was added to a solution of $MoOCl_3 \cdot 2DMSO$ in 34 ml of DMSO, prepared by the reaction of 5.55 g of $MoCl_5$ with 4.2 ml of DMSO. Toluene was preliminarily distilled off from the solution of sodium polyphenylsiliconate. The reaction was performed at room temperature for 8 h and then at 60°C for 4 h. The polymer was isolated similarly to the previous synthesis. Yields: polymer 6.30 g (58.3%),

water-soluble products 4.12 g (39.4%), and NaCl 3.50 g (99.7%).

Synthesis of polymolybdenophenylsiloxane, sample PMoPS-3, was performed similarly to the synthesis of PMoPS-1. To isolate the polymer, excess anhydrous $CaCl_2$ was added to completely bind DMSO, and toluene was distilled off. The polymer was dried to constant weight at 100°C (20 mm Hg). Yield of PMoPS-3 11.30 g (99.1%), yield of NaCl 3.81 g (99.5%).

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