



INTERACTION OF POLYORGANOSILSESQUIOXANES WITH SULFUR

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Abstract

The interaction of elemental sulfur with polyvinyl- and polyphenylsilsesquioxanes was accomplished to give the products which partially lost solubility in organic solvents. The composition and structure of the isolated compounds were investigated. In the IR spectra, the absorption bands associated with the double bond disappeared, while new bands indicating the addition of sulfur emerged. A slight shift of the first reflex on the XRD pattern with a noticeable change in the volume of the coherent scattering region also indicated the interaction of sulfur with siloxanes. The thermogravimetric analysis (TGA) of the polyvinylsilsesquioxane product showed the presence of a significant exo-effect on the DTA curve, which is associated with the oxidation of the sulfur-containing moiety.

Key words: polyphenylsiloxane, polyvinylsiloxane, sulfur, thermogravimetric analysis.

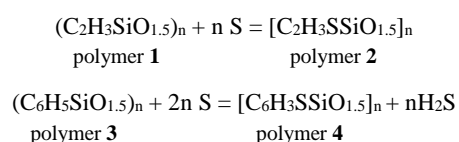
PVSQ	→	IR spectroscopy, NMR spectroscopy, elemental analysis, diffractometric analysis, TGA and DTA
PVSQ + S	→	
PPSQ	→	
PPSQ + S	→	

Introduction

The creation of materials for electrochemical devices (accumulators, batteries, capacitors, *etc.*) based on the derivatives of heavy metal sulfides and silicon-containing matrices is one of the most important directions of modern applied chemistry [1–3]. It is known that polyorganosiloxanes are used to produce electroactive membranes for lithium-ion batteries [4]. Terpenoids were shown to be one of the most promising classes of natural compounds in the field of polymer synthesis [5, 6]. The addition of elemental sulfur to unsaturated compounds has been studied for a long time [7], and recent investigations have demonstrated that the addition of sulfur and silicon hydrides to terpenoids affords sulfur-containing polyorganosiloxanes [8]. Taking this into, this work was devoted to the investigation of the addition of elemental sulfur to polyorganosiloxanes.

Results and discussion

The reactions were carried out by heating a mixture of polyvinylsilsesquioxane (PVSQ, polymer **1**) or polyphenylsilsesquioxane (PPSQ; polymer **3**) with elemental sulfur at 160–180 °C in melt according to the following schemes:



The resulting polymers (**2** and **4**) are brittle, easily rubbed solids of light-brown and light-gray color. Polymer **2** is insoluble in organic solvents, while polymer **4** is soluble in dimethyl sulfoxide. The observed deviations of the found values of the element contents from the calculated ones (see the Electronic supplementary information (ESI)), as was shown earlier [9], are caused by the presence of hydroxy groups at the silicon atom.

The IR spectrum of polymer **2** revealed the following differences from that of polymer **1**: 1) the appearance of an absorption band at 3400 cm^{−1} (O–H bond); 2) the appearance of absorption bands at 2923 cm^{−1} and 2854 cm^{−1} (ethyl C–H bonds); 3) the absence of an absorption band at 1531 cm^{−1} (vinyl C–H bond); 4) the appearance of absorption bands at 1456 cm^{−1} and 1448 cm^{−1} (ethyl C–H bond); 5) a slight shift in the absorption band corresponding to the stretching vibrations of the Si–C bond; 6) the disappearance of absorption bands at 1043, 1006, 968 cm^{−1} and their merging into a common one. The absorption bands at 1006 and 1043 cm^{−1} are attributed to the Si–O bond vibrations in the eight-membered silsesquioxane ring, while the absorption band at 968 cm^{−1} corresponds to the stretches of terminal Si–O groups [10]. The observed changes in the IR spectrum of polymer **2** can be explained by the fact that PVSQ interacts with elemental sulfur in several directions: 1) the cleavage of the double bond with the formation of polysulfide bridges; 2) the cleavage of Si–O–Si bonds. The cleavage of Si–O–Si bonds under the action of sulfur is likely to proceed with the formation of Si–S bonds, as was evidenced by the formation of a single absorption band at 1000–1100 cm^{−1}. In the case of the interaction of PPSQ with elemental sulfur (polymer **4**), significant changes in the C–H oscillation region

were noted in the IR spectrum: the introduction of sulfur led to the disappearance of absorption bands at 3139 and 3030 cm^{-1} . A change in the IR spectrum of the product of interaction of PPSQ with sulfur (polymer 4) can be explained by substitution of the hydrogen atoms for the sulfur ones at the second and sixth carbon atoms, similar to the process of proton substitution in aniline with sulfur [11].

The results of XRD analysis were used to calculate the size, cross-section and volume of the coherent scattering region (CSR) for polymers 1–4 (Table 1) according to Refs. [12, 13]. The diffractometry data revealed an increase in the interplanar distance, which is apparently associated with the interaction of sulfur and PPSQ, and the presence of sulfur between the chains [14]. According to Ref. [15], a decrease in the volume of CSR indicates an increase in the degree of amorphousness of the polymer itself and therefore an increase in its heterogeneity. TGA was used to study the sulfur–PVSQ mixture obtained by mixing and grinding at 600 rpm (grinding time: 10 min) to better understand the interaction process with increasing temperature. Three exo-effects were observed for the mixture sample: the first one was observed at 310 °C (max), the second exo-effect was observed at 436 °C, and the third one was observed at 608 °C. The weight loss of the first exo-effect was about 29–30%, which probably corresponds to the general process of interaction of sulfur and vinyl groups and their simultaneous oxidation. This is also confirmed by the results of the ^{29}Si solid-state NMR spectroscopic studies, which revealed a signal at 100 ppm corresponding to SiO_2 . According to the elemental analysis of the mixture, separately heated to 310 °C, the silicon content is 30.1%, and that of sulfur is 4.2%. This corresponds to the gross formula $[(\text{SiO}_2)_{0.87}(\text{C}_2\text{H}_3\text{SiO}_{1.5}\text{S})_{0.13}]$. The exo-effect at 436 °C corresponds to the oxidation of the addition products. The exo-effect at 608 °C corresponds to the oxidation of the remaining vinyl groups.

Table 1. X-ray diffraction data

Polymer	d_{001} , nm	S_b , nm^2	L_{CSR} , nm	V_{CSR} , nm^3
1	0.92	0.69	2.63	1.83
2	0.95	0.72	3.19	2.30
3	1.23	1.12	6.19	6.95
4	1.25	1.15	3.89	4.49

d_{001} is the interplanar distance between polymer chains;

S_b is the cross-sectional area of the chain,

L_{CSR} is the size of the coherent scattering region of the polymer chain,

V_{CSR} is the volume of coherent scattering.

Conclusions

Hence, PVSQ and PPSQ react with sulfur to form the polymers with a Si:S ratio of 1:1. Based on the IR spectroscopic and diffractometry data, it was shown that the interaction of PVSQ with sulfur proceeds with the cleavage of the double bond and the formation of sulfide bridges in polythioethylsilsesquioxane. In the case of PPSQ, the interaction presumably occurs at the second and sixth carbon atoms with the formation of polythiophenylsilsesquioxane.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: [the experimental details, IR and NMR spectra, TGA and XRD data](#). For ESI, see DOI: 10.32931/ioXXXXx.

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