AGEENKOV ALEKSANDR

«Eugenol-containing oligosilsesquioxanes and coatings based on them»

Abstract

Relevance of the Research Topic. The introduction of novel functional substituents at the silicon atom in organosilicon compounds is a promising task in both polymer chemistry and materials science. Addressing this challenge will expand the scope of their application as versatile building blocks in the molecular design of new compounds and enable the development of novel polymeric materials with tailored functional properties. For instance, incorporating eugenol fragments into polymer structures can yield materials with valuable characteristics, such as resistance to macro- and microorganism proliferation, anticorrosion properties, flame retardancy, and others. In the case of organosilicon compounds, eugenol functionalization can be achieved through hydrosilylation and Pierce-Rubinsztajn reactions.

Moreover, over the past decade, the functionalization of organosilicon compounds via hydrothiolation has gained popularity as a simple and efficient method for introducing unsaturated compounds of synthetic and natural origin into their structure. Of particular scientific interest is the study of the synthesis features of both eugenol-functionalized monomers and the resulting polymers. It should be noted that the organic substituent at the silicon atom, as well as the polycondensation conditions of organotrialkoxysilanes, significantly influence the composition, structure, and properties of the resulting oligoorganosilsesquioxanes. Investigating this influence is of both theoretical and practical importance for further control over polymer structure and, consequently, the properties of the final polymeric materials.

The synthesized eugenol-functionalized organosilicon polymers may find applications as standalone film-forming materials for specialized adhesive coatings or as components in polymer composites with other organic polymers, particularly epoxies. The obtained results open new prospects for the use of organosilicon polymers as functional polymeric materials with enhanced performance characteristics.

Degree of Research Development. Previous studies have demonstrated the influence of polycondensation conditions, length, and bulkiness of organic substituents at the silicon atom on the synthesis, structure, and properties of oligoorganosilsesquioxanes. Additionally, conditions for the secondary functionalization of linear organosilicon compounds with eugenol via hydrosilylation and Pierce-Rubinstein reactions have been reported. The preparation of composites based on eugenol-functionalized linear polyorganosiloxanes and epoxy resins has also been investigated.

Objects of the Present Study. The objects of this research include:

- functionalization of 3-mercaptopropyltrimethoxysilane with eugenol via hydrothiolation;
- synthesis of oligoorganosilsesquioxanes based on the secondarily functionalized monomer through hydrolytic and active medium polycondensation;
- their application as film-forming agents for functional coatings.

Research Objective. The aim of this work is to synthesize novel eugenol-functionalized oligoorganosilsesquioxanes for the development of functional coatings. To achieve this goal, the following tasks were addressed:

- synthesis of *S*-[(p-hydroxy-m-methoxy)phenylpropyl]mercaptopropyl trimethoxysilane via UV-initiated hydrothiolation of eugenol with 3-mercaptopropyl trimethoxysilane;
- synthesis of oligo-*S*-[(p-hydroxy-m-methoxy)phenylpropyl]mercaptopropyl silsesquioxanes from the obtained monomer using hydrolytic and acid-hydrolytic polycondensation methods;
- investigation of the influence of the new organic substituent at the silicon atom and synthesis conditions on the structure and properties of the resulting oligosilsesquioxanes;
- study of the compatibility of the synthesized oligoorganosilsesquioxanes with epoxy resin and determination of conditions for forming crosslinked structures;

- preparation and characterization of coatings based on the synthesized oligoorganosilsesquioxanes and their composites with epoxy resin.

Scientific Novelty of the Dissertation. The scientific novelty of the dissertation lies in the following:

- first synthesis and characterization of the monomer *S*-[(p-hydroxy-m-methoxy)phenylpropyl]mercaptopropyl trimethoxysilane via UV-initiated hydrothiolation;
- first synthesis and characterization of oligo-*S*-[(p-hydroxy-m-methoxy)phenylpropyl]mercaptopropyl silsesquioxanes from the obtained monomer using hydrolytic and acid medium polycondensation;
- study of the influence of the organic substituent at the silicon atom in *S*-[(p-hydroxy-m-methoxy)phenylpropyl]mercaptopropyl trimethoxysilane and its polycondensation conditions on the structure and properties of the resulting oligosilsesquioxanes;
- first preparation and characterization of unfilled hybrid epoxy-organosilicon composites and coatings based on the synthesized oligomers.

Theoretical and Practical Significance. The theoretical and practical significance of the dissertation results stems from:

- Expanding the range of functionalized organotrialkoxysilanes through the synthesis of the previously uncharacterized *S*-[(p-hydroxy-m-methoxy)phenylpropyl]mercaptopropyl trimethoxysilane, which serves as a molecular spacer $-(CH_2)_3-S-(CH_2)_3-$ linking the trimethoxysilyl $(MeO)_3Si-$ and p-hydroxy-m-methoxyphenyl $-C_6H_3(OH)(OMe)$ fragments.
- The presence of four −OMe groups and one −OH group in the synthesized organotrialkoxysilane, enabling its use as a versatile building block in reactions such as dehydrogenative coupling, *O*-demethylation, *O*-glycidylation, allylation, alkoxylation, hydroxyethylation, and acylation for further functionalization or polycondensation.
- Development of novel, previously undescribed oligosilsesquioxanes applicable as homo-oligomers or oligomer mixtures for functional polymer composites.

- Elucidation of the influence of the new organic substituent at the silicon atom on the structure, composition, and properties of the resulting oligosilsesquioxanes.
- Practical application in high-temperature-curable epoxy-organosilicon composites and corrosion-resistant coatings.

Methodology and Research Methods, Reliability of Results. The following methods were employed:

- NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si);
- FTIR spectroscopy;
- GC-MS;
- MALDI-TOF mass spectrometry;
- GPC;
- DSC;
- TGA;
- Optical wedge interferometry;
- SEM;
- Potentiodynamic corrosion resistance studies;
- Standardized methods for adhesive coating characterization.

Statements Submitted for Defense:

- hydrothiolation of eugenol with 3-mercaptopropyl trimethoxysilane;
- synthesis of oligosilsesquioxanes with a novel eugenol-functionalized organic substituent at the silicon atom;
- influence of the organic substituent on the composition and structure of oligosilsesquioxanes formed during polycondensation;
- preparation of epoxy-organosilicon composites, coating formation mechanisms, and their functional properties.