ANNOTATION

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Synthesis, structure, properties and application of new oligomeric silsesquioxanes, phosphazenes and siloxanephosphazenes

Relevance of the research topic. Organoelement silicon- and phosphorus-containing oligomers and polymers are increasingly important and find application in virtually all areas of the national economy – from mechanical engineering and electronics to medicine and agriculture. This primarily applies to polysiloxanes and polyphosphazenes, which are used to obtain and manufacture polymer composite materials with high dielectric properties, fire and heat resistance, radio transparency, and bioinertness. Previously, the Department of Chemical Engineering of Plastics at the D.I. Mendeleev University of Chemical Technology of Russia developed simple and effective methods for synthesizing oligomeric organosilsesquioxanes (OSSO) and oligomeric cyclic phosphazenes (OCP), which contain various functional groups in organic radicals attached to silicon and phosphorus atoms. These oligomers have found application as binders and modifiers for organic polymers (acrylic, epoxy, etc.) to enhance the physicochemical and mechanical properties of composite materials based on these oligomers. These studies revealed the need to adjust the composition and properties of these oligomers for specific applications. A distinctive feature of OSSO and OCP is their polyfunctionality: the content of functional groups in the molecule can exceed 10, which, when silsesquioxane or phosphazene cycles are incorporated into the structure of the three-dimensional network formed during curing, leads to significant changes in the physicomechanical properties of the polymeric materials. Possible options for regulating the properties of such composites include varying the nature and number of functional groups in the OSSO and OCP used, as well as introducing flexible linear siloxane or phosphazene bridges between the rigid fragments of silsesquioxanes and cyclophosphazenes. By the time this work begins, significant scientific and practical advances have been made in the synthesis and analysis of organosilicon and organophosphorus oligomers and polymers. However, data on ways to control the structure and composition of functional oligosilsesquioxanes, particularly copolymers containing silsesquioxane and linear siloxane blocks, remain lacking. The methods for synthesizing and the properties of linear functionalized oligophosphazenes remain largely unstudied.

The aim of this dissertation is to develop methods for synthesizing functionalized oligosilsesquioxanes, linear oligophosphazenes, and polysiloxanephosphazenes, and to determine their composition, structure, and potential applications for producing polymer composite materials with improved properties.

To achieve the aim of the study, the following **tasks** were set: (1) determination of optimal conditions for the hydrolytic and acidohydrolytic polycondensation of organotrialkoxysilanes, eliminating both the possibility of three-dimensional polymer formation and side reactions of functional groups; (2) establishing the composition, structure, and methods for regulating the properties of the resulting oligosilsesquioxanes; (3) synthesis of new functionalized linear oligophosphazenes with controlled phosphazene chain length; (4) development of methods for synthesizing oligo- and polysiloxanephosphazenes via hydrosilylation of oligophosphazenes with allyl groups in organic radicals bound to phosphorus atoms.

Scientific Novelty:

(1) Methods have been developed for synthesizing new organosilsesquioxane and linear phosphazene oligomers, in which more than 100 individual compounds have been identified. (2) Optimal conditions for the hydrolytic and acidohydrolytic homo- and copolycondensation of organotrialkoxysilanes with amine, methacrylic, and phosphazene groups in organic substituents have been established. The acidolysis and hydrolysis stages are shown to be independent of the nature of the substituents, but they have a significant influence on the completion of polycondensation and the composition of the resulting oligosilsesquioxanes, the total content of ladder and cage-like fragments in which can reach 95%. (3) During the hydrolytic copolycondensation of the corresponding trialkoxysilanes, side reactions of methacrylic groups with amine groups, such as the Michael reaction, partial hydrolysis of ester groups, and the formation of zwitterionic structures, have been identified. (4) Methods have been developed for the synthesis of linear oligodichlorophosphazenes with controlled chain lengths by living cationic polymerization of N-trimethylsilyltrichlorophosphoranimine at normal temperature or by equilibrium polycondensation of trichlorophosphazodichlorophosphonyl at 250°C. The most probable mechanisms for these reactions, including the formation of active transition four-center states, have been proposed. (5) An equation linking the molar ratio of N-trimethylsilyltrichlorophosphoranimine and PCl_5 has been derived, allowing for the accurate calculation of the molecular weight of the resulting oligo- or polydichlorophosphazenes. (6) Polysiloxanephosphazenes capable of forming three-dimensional structures with adjustable network resolution and interstitial chain sizes were synthesized and characterized by the reaction of allyl-containing oligophosphazenes with hydride- and α,ω-dihydridesiloxanes. (7) Under hydrosilylation conditions of the allyl groups of organic diphosphonylamine in the presence of a Karstedt catalyst, silylation of the NH group with triethoxysilane was observed, forming a silicon–nitrogen bond.

Theoretical and Practical Significance. The established patterns of reaction for the formation of oligosilsesquioxanes, linear oligophosphazenes, and polysiloxanephosphazenes open up new possibilities for the synthesis of compounds of this class and significantly expand existing understanding of the chemistry of polysiloxanes and polyphosphazenes. The synthesized oligomers have been successfully used as modifiers and binder components for polymer composite materials with improved properties. They are of interest as materials for biomedical applications (implants, drug carriers), ion-exchange resins, and extractants for rare and trace elements. A number of known, but not obvious, chemical reactions for organoelement compounds have been discovered, such as the interaction of amino and methacrylic groups contained in organic radicals attached to silicon atoms via a Michael reaction.

Thesis proposals: (1) Development of methods for the synthesis of functionalized oligosilsesquioxanes, linear oligomeric phosphazenes, and siloxanephosphazenes. (2) Results of studies of the structure, composition, and properties of these compounds. (3) Comparison of the formation patterns of various types of oligomers, determination of the spectral characteristics of synthesized previously undescribed compounds and their mixtures, and evaluation of the physicochemical properties of the resulting oligomers and polymers. (4) Identification of the most promising applications of the synthesized oligomers and polymers as modifiers and binders for polymer composite materials.