

Synthesis and conversions of amino- and methacrylate-containing oligoorganosilsesquioxanes

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The relevance of the research topic and the degree of its elaboration. Oligomeric organosiloxanes and silsesquioxanes, depending on the nature of the functional groups, can be used to effectively modify the corresponding polymer composites and give them improved performance characteristics. Thus, the presence of methacrylic groups in substituents at silicon atoms of silsesquioxane oligomers allows them to be used in acrylic compositions, increasing their hydrophobicity and reducing polymerization shrinkage during curing. Another important characteristic is the high adhesion properties of the cured composite to various substrates. Therefore, it seems promising to obtain siloxane and silsesquioxane oligomers containing, along with methacrylic, other functional groups (amine, carboxyl) capable of covalent binding with epoxy, methacrylic and other binders of polymer composite materials.

At present, in the production of modified polymeric materials, the need has emerged to further improve the characteristics of both the organosilicon oligomers themselves and the composites modified by them.

The purpose of this thesis was to develop methods for the synthesis of mixed amino, carboxyl and / or methacrylate-containing oligosilsesquioxanes with an adjustable ratio of functional groups, as well as to assess the physical and mechanical characteristics of the cured dental materials modified by them.

To achieve this goal, it was necessary to solve the following tasks:

- to synthesize mixed oligosilsesquioxanes containing aminopropyl and methacrylate-containing groups in organic radicals at silicon atoms;
- to synthesize carboxyl-containing oligosilsesquioxanes by the reaction of aminopropyl radicals at silicon atoms with maleic anhydride;
- to study the chemical stability and transformation of oligosilsesquioxanes with the indicated functional groups;
- modify polymer compositions for dental filling materials with mixed methacrylate-containing oligosilsesquioxanes.

Scientific novelty

1. Methacrylate-containing silsesquioxane-siloxane oligomers with $M_w = (2-20) \times 10^3$ synthesized by acidhydrolytic copolycondensation 3-methacryloxypropyltrimethoxysilane with methylphenyldimethoxysilane, dimethyldimethoxysilane and dimethyldiethoxysilane;

2. The optimal conditions for the synthesis of amine-containing oligosilsesquioxanes soluble in organic solvents by hydrolytic (co) polycondensation of alkoxy silanes in ethanol have been found;

3. Under conditions of hydrolytic copolycondensation 3-aminopropyltriethoxysilane and 3-methacryloxypropyltrimethoxysilane, a side reaction of amino groups with methacrylic ones (Michael reaction) was established; this transformation was confirmed by the model reaction of aminopropylsilane with methyl methacrylate;

4. New oligosilsesquioxanes with carboxyl and methacrylic groups were synthesized by hydrolytic copolycondensation of a monomaleamide derivative of 3-aminopropyltriethoxysilane with 3-methacryloxypropyltrimethoxysilane;

5. The high efficiency of methacrylate-containing silsesquioxane-siloxane oligomers as modifiers of dental filling compositions was shown.

The theoretical and practical significance of the work

The results obtained made it possible to expand the existing understanding of the mechanism of the Michael reaction, extending them to the interaction of aminopropyl and methacryloxypropyl groups bound to silicon atoms.

The synthesized methacrylate-containing silsesquioxane-siloxane oligomers proved to be effective modifiers of the physical and mechanical properties of dental polymer compositions. Silsesquioxane oligomers with aminopropyl and phenyl substituents were used as hardeners-modifiers of epoxy oligomers.

Defense provisions:

- synthesis of methacrylate-containing silsesquioxane-siloxane oligomers by acidhydrolytic copolycondensation of tri- and difunctional alkoxy silanes;

- synthesis of mixed (aminopropyl) phenylsilsesquioxane oligomers by hydrolytic copolycondensation of 3-aminopropyltriethoxysilane and phenyltrimethoxysilane in ethanol;

- determination of the structure of the products of joint hydrolytic polycondensation of 3-aminopropyltriethoxysilane and 3-methacryloxypropyl-trimethoxysilane according to NMR spectroscopy data;

- obtaining a monomaleamide derivative of 3-aminopropyltrimethoxysilane;
- synthesis of chemically stable mixed oligosilsesquioxanes containing methacrylic and monomaleamide groups;
- the possibility of improving the physical and mechanical properties of polymeric dental compositions by modifying synthesized methacrylate-containing oligomeric silsesquioxane-siloxanes.