



Streszczenie w języku angielskim

The field of dendrimer chemistry has been continually evolving, driven by the diversity of structures that can be obtained. Dendrimers, characterized by a spherical structure with numerous surface functional groups, exhibit enhanced physicochemical properties in comparison to their counterparts with fewer identical groups. Various polyamidoamine, carbosilane, and carbosiloxane groups serve as dendrimer cores. In recent years, there has been growing interest in the use of specific organosilicon compounds, so-called silsesquioxanes, as dendrimer cores. These three-dimensional structures feature well-defined Si-O-Si connections, forming the core with organic groups anchored on the surface. Therefore, the nature of these organic-inorganic structures defines them as hybrid compounds exhibiting interesting physicochemical properties which determine their subsequent wide use in materials chemistry, medicine, industry, but also in everyday life.

The doctoral thesis, titled "*Dendritic Systems Based on Functionalized Silsesquioxanes – Synthesis and Characterization*", focused on designing and developing synthesis protocols for dendrimers with different silsesquioxane cores - monofunctional T_8 (cubic) with isobutyl and phenyl inert groups, as well as di- and tetrafunctional double-decker silsesquioxanes. Selected physicochemical properties of the compounds were characterized. This doctoral dissertation is composed of four publications (**P1** – **P4**) covering the synthesis and characterization of silsesquioxane dendrimers with different dendrons: vinyl- and chloromethyl-substituted dendrimers (**P1**), carbosilane dendrimers (**P2**), ferrocene-substituted dendrimers (**P3**), and polyol dendrimers (**P4**). **P3** describes ferrocene dendrimers based only on tetrafunctional DDSQ core.

The first publication (**P1**) is focused on the development of a synthetic route to low-generation vinyl- and chloromethyl-substituted dendrimers (G1 and G1.5) using a synthetic protocol based on condensation and hydrosilylation reactions. Unexpectedly, during the first stage of research, a new type of double-decker silsesquioxane, closed on one side of the corner, was obtained which was confirmed by XRD analysis. In the second stage of studies on the hydrosilylation process, the influence of the type of catalyst and reaction temperatures on the efficient conditions enabling selective obtaining of the β -addition product - crucial in dendrimer synthesis - were verified. The selection of the introduced reactive groups (vinyl- and chloromethyl-) was the intended goal to examine the possibility of their further use due to the ease of modification.

The second publication (**P2**) described the synthesis of carbosilane-substituted dendrimers using a custom-designed procedure based on a sequence of hydrosilylation and reduction reactions. As a part of these studies, the location of the Si-H bond in the reagents' structures was verified in terms of the impact on selectivity of the hydrosilylation process. The type of reducing agent was also revised and various methods of purifying of the obtained products were developed, depending on the reagents used, i.e. the silsesquioxane structures. Additionally, the possibility of modifying the Si-H bond present in the new dendrimers of the G.1 generation was examined using the hydrosilylation reaction in order to functionalize it, as well as to further expand the dendrimer by using the developed "*one-pot*" method.

The third publication (**P3**) was devoted to gaining dendrimers with ferrocene substituents and a double-decker silsesquioxane core. An additional aspect of the research was the characterization



of the compounds in terms of their thermal stability and solubility in basic organic solvents. Moreover, due to the ferrocene groups present in the structure, the obtained systems were tested for reduction-oxidation properties using cyclic voltammetry (CV) during an internship in the group of prof. Pilar García Armada, as a part of the scholarship from the *Excellence Initiative – Research University* project. Within conducted studies, platinum electrodes modified by ferrocene dendrimers were prepared and characterized by cyclic voltammetry (CV) and electrochemical impedance techniques (EIS).

The fourth publication (**P4**) concerned the synthesis of polyol dendrimers with different silsesquioxane cores. For this purpose, the developed synthetic route explored the sequence of catalytic reactions: hydrosilylation, *O*-silylation and hydrosilylation. During the tests, the influence of the structure of olefins with hydroxyl groups used in the research was verified. The physicochemical properties of the obtained dendritic systems were verified in terms of the amount of organic substituents and the type of silsesquioxane core. To isolate these compounds, three purification methods were developed and they were dependent on the type of dendrimer core. Also, the stability of the G1.5 systems in atmospheric conditions was verified.

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The optimized synthetic procedures presented in publications **P1 – P4** resulted in obtaining 39 dendritic systems, 36 of which are novel. The structures were spectroscopically confirmed, demonstrating unique physicochemical characteristics. It was proved that such systems with a defined structure possess their individual physicochemical features due to the various functionalities present in their structure, as well as different types of silsesquioxane cores, which determined the specific approach in their preparation. These studies contribute to the ambitious challenges in materials chemistry, providing a library of novel compounds merging dendrimer and silsesquioxane properties for potential diverse applications. The work aligns with the ongoing exploration and development of hybrid dendrimer structures, holding promise for future discoveries in this exciting field of chemistry.