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“Functionalized linear poly(silsesquioxanes) - synthesis, properties and applications”

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SUMMARY

My doctoral thesis on "Functionalized linear poly(silsesquioxanes) - synthesis, properties and applications" are focussed on linear poly(silsesquioxanes) with a double silicon-oxygen main chain (LPSS). These polymers are a very interesting material for studying the relationship between the properties of macromolecules and their structural structure, but in fact they are the least-known group of organosilicon compounds built of silsesquioxane units. The aim of my work was to develop an efficient method for their synthesis, allowing for preparation of macromolecules with a low number of structural errors. I have focussed my studies on the preparation of linear poly(silsesquioxanes) bearing side vinyl groups at silicon atoms (LPSS-Vi), that could be used as precursors in the synthesis of various organofunctional LPSS. Another key task of my work was to examine a variety of synthetic routes for modification of LPSS-Vi (e.g. thiol-ene addition, Mizoroki-Heck reaction) to obtain new polymeric derivatives.

During the research, a new method for the synthesis of poly(vinylsilsesquioxanes) was developed (through *in situ* polycondensation of 2,4,6,8-tetravinylcyclotetrasiloxane-2,4,6,8-tetraol). It allowed for preparation of the desired linear macromolecules with high yield. The influence of various factors on the course of condensation reactions and the structure of products was also examined. The properties of the obtained materials were compared with macromolecules synthesized according to other procedures, such as stepwise coupling polymerization (SCP) and hydrolytic polycondensation. Attempts have also been made to obtain LPSS with side phenyl groups as well as 3-mercaptopropyl substituents. A significant dependence of the result of polycondensation *in situ* on the type of functional groups at silicon atoms, and stereoelectronic effects they exert, was demonstrated. The main analytical technique applied for studies on the course of the polycondensation reaction and the structure and molecular weight of the LPSS products was mass spectrometry with matrix-assisted laser desorption/ionization (MALDI TOF). The products were also characterized by NMR and FTIR spectroscopies.

Development of advanced technologies utilizing hybrid polymeric materials requires new solutions that enable control of the properties and set new areas of applications. The choice of research objective made concerning the application of LPSS was linked to their specific features, resulting directly from the main chain structure and the specific morphology of macromolecules. Their chemical resistance, good solubility and related film-forming capabilities are also very important. It should be emphasized that the unique geometric structure of LPSS allows for the formation of well-defined, spatially ordered structures. Consequently, an appropriate modification of LPSS can result in completely new materials with unique physical and chemical properties.

Physicochemical properties of surfaces (e.g.: wettability, type of functional groups, surface charge, roughness) can be extremely important in the case of materials designed for specialized applications, including bioengineering. Therefore, one of the goals of my research was to prepare new, functionalized hybrid materials that could be used for surface modification and preparation of thin polymer films (PSAM). The obtained poly(vinylsilsesquioxanes) were modified by thiol-ene addition of low molecular weight compounds (thioglycolic and 3-mercaptopropionic acids, methyl thioglycolate, N-acetylcysteine, cysteine hydrochloride, glutathione). Physicochemical properties of all the prepared materials were examined as well as their adsorption on the surface of various solid substrates (mica, glass, silicon). The ability of functionalized LPSS to form well-organized layers of high hydrophilicity, as well as good thermal and solvolytic resistance, was demonstrated. The reason for the observed phenomena was the unique structure of hydrogen bonds, which was indicated by ATR-FTIR analysis.

LPSS-Vi were also used for the synthesis of systems containing optically active pyrene substituents (LPSS-Py). Mizoroki-Heck reaction was applied as the synthetic method. The characteristic structure of linear poly(silsesquioxanes) is responsible for the unique optical activity of the materials which exhibited only an intense emission of excimer fluorescence, both in solutions and in solid state. The unique photoptic properties, high thermal resistance, good solubility and processability of LPSS-Py make them an interesting hybrid material for optoelectronics applications. These systems were also used as energy donors in FRET processes. In summary, design of new, potential areas of application for linear poly(silsesquioxanes) allowed for a wider use of these hybrid polymers.