

Silsesquioxanes with oligomeric cage-structures

Silsesquioxanes appear in polymer and in some oligomeric structures. This work aimed at the synthesis of functionalized oligomeric silsesquioxanes in order to combine them to large oligoblock silsesquioxanes. Therefore several new silsesquioxanes with different side chains were prepared. Basic principle of the preparation is the acid catalyzed hydrolysis of trichloro- and trialkoxysilanes, resp., followed by condensation in methanol. It has to be noted that this method is generally not applicable to all silsesquioxanes.

Oxiranyl functionalized silsesquioxanes were synthesized by the Prileschajew reaction of olefinic silsesquioxanes. The thioether species were synthesized by radical addition of thiols to olefinic silsesquioxanes. A typical example for the synthesis of oligoblock silsesquioxanes starting from such functionalized silsesquioxanes is the adaption of the latter type of reaction by adding silsesquioxanes with one thiol function to silsesquioxanes with vinyl side-chains. Octavinylsilsesquioxane and monothiopropyl-hepta-n-propyl-silsesquioxane react using this method to give the so called nonablock silsesquioxane (Fig. 1).

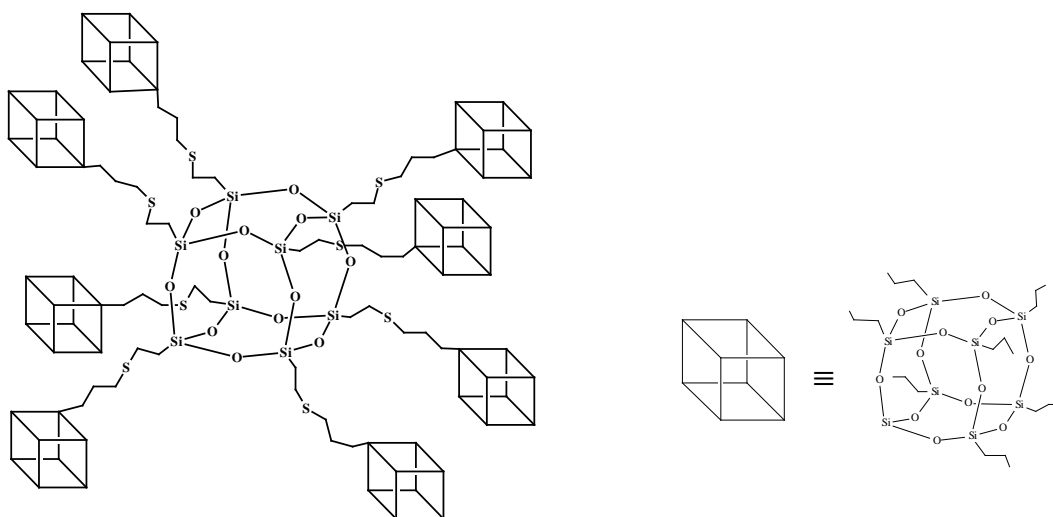


Fig. 1: nonablock silsesquioxane

The resulting compound consists of 72 silicon-, 108 oxygen-, 208 carbon-, 8 sulfur- and 472 hydrogen-atoms. It was characterized by ^{29}Si -, ^1H - and ^{13}C -NMR-spectroscopy giving information on its structural features as well as confirming its composition (number of distinguishable Si-atoms and organic residues). The expected molecular mass was confirmed by MALDI-TOF MS. Elemental analysis and IR-spectroscopy support these results. Mostly the products were purified by preparative HPLC.