THE ELECTROCHEMICAL SYNTHESIS OF DENDRITIC POLYMETHYLSILANE

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Branched polysilanes are superior to linear polysilanes, due to their optical properties, stability and ceramic yield for production of SiC. Those properties are altered by polymer sizes. Understanding of the synthesis mechanism and the structure of obtained polymers is therefore crucial for design of the branched polysilanes for industrial applications. A synthesis by electropolymerization from chlorosilanes offers, compared to reduction with liquid alkali metals, safer and more controlled conditions. Regardless the potential of the electrochemical synthesis, the polymerization mechanism and the structure of the obtained polymers have been barely discussed.

The dendritic polymethylsilane molecules were synthesized by the electroreduction of methyltrichlorosilane monomers. Using a constant current electrolysis and a cyclic voltammetry we showed that a single polymerization pathway, involving the reduction of monomers to form silyl anions and their addition to the growing polymer, exists. This is in contrast with previous assumption of the Si-Cl bond reduction on polymeric species [1]. The polymers were synthesized under two conditions, with strong and weak ionic electrolytes. A quantitative analysis of ^{29}Si solid state NMR spectra revealed that the structure is not regularly branched into three directions at each monomer unit, but it contains a large number of linear segments (defects). Those defects have severe impact on the macromolecule size. The size of a regular dendrimer is sterically limited; after certain generation the volume required for attaching the next generation of monomers exceeds the available volume [2], the introduction of defects is at this point necessary to propagate the polymer growth with the hyperbranched dendritic structure. Combining experimental values obtained by DLS and density measurements with a structural model considering branching irregularities, we showed for two synthesized polymers that the inclusion of the defects allows the dendritic polymer to exceed the sterical limitations. The final size depends on a relative amount of the branching defects [3].

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