

Synthesis and Thermal Analysis of Mono-Substituted POSS Polymers

Elda Markovic, Stephen Clarke

Mawson Institute/University of South Australia
GPO Box 2471, Adelaide, South Australia, 5001, Australia
Elda.Markovic@unisa.edu.au; Stephen.Clarke@unisa.edu.au

Extended Abstract

Polyhedral oligomeric silsesquioxanes, usually referred to as POSS are unique compounds, three-dimensional nanobuilding blocks that can be used to create a wide variety of hybrid materials, where precise controls of nanostructures are required (Markovic et al, 2011, Sanches et al, 2001). From the microscopic viewpoint, the characteristic nanoscopic size of the POSS molecule (1.5 nm) is comparable to the dimensions of polymeric segments and the incorporation of POSS moieties into linear polymer chains and/or polymer networks will modify the local molecular interactions, local molecular topology, and the resulting polymer chain and segment mobility. These modifications are demonstrated in the macroscopic physical properties, such as glass transition temperature and thermal stability,

Mono-substituted poly octahedral silsesquioxanes (POSS) are represented by general formula $R'R_7Si_8O_{12}$. These materials have only one reactive group that allows the opportunity of further functionalization, while the other corners are inert. This allows incorporation of these monomers into organic-inorganic modifying only the surface of the hybrids. Polymerization at the single reactive site results in the synthesis of linear polymers containing nanosized monodisperse inorganic POSS cluster pendant to an organic polymer backbone.

In this paper mono-substituted POSS materials are synthesised by “corner-capping” reactions as shown by Feher et al. (1991) This synthesis yielded a range of mono-functionalized POSS as the only products that possess mono-functional reactive R' groups and a number of the inert R groups. These mono-functionalized POSS compounds were further modified by reactions of R' group. Such mono-functional POSS were further functionalised via hydrosilylation reaction that introduced a number of functional groups, which created the mono-functional POSS macromonomers. These macromonomers were employed as suitable precursors that were used in polymerisation reactions. Various polymerisation methods were introduced in order to prepare a series of nanomaterials where the POSS molecules were incorporated into the linear backbone.

A series of the mono-functional POSS macromonomers bearing various inert organic groups (Et, i-Bu, i-Oct, Cp, Ch, Ph) and only one S-H functionality were synthesised and further functionalised. These macromonomers were then polymerised in order to obtain a number of different polymers, such as POSS-Polyethylene Glycols (POSS-PEG), POSS-Poly Urethanes (POSS-PU, POSS-Poly Methyl Methacrylates (POSS-PMMA). These materials were analysed for their purity by ¹H NMR, ²⁹Si NMR and FTIR spectroscopy methods.

Thermal study of mono-substituted POSS-PEG macromonomers showed improved thermal decompositions of materials when compared with the starting Si-H POSS. In addition, the TGA of the various chain length mono-substituted POSS was observed to increase as the PEG chain increased, and had similar behaviour of the octa-substituted counterparts (Markovic et al., 2008)

POSS-PU were synthesised from the mono-functional POSS monomers, poly(ethylene adipate), tolylene 2,4 diisocyanate terminated prepolymer and PEG homopolymers. In order to obtain POSS end-capped PEGs. The thermal studies of these materials revealed altered degradation and melting temperatures when compared to mono-substituted hybrid materials.

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