

## Polyoligomeric Silsesquioxanes Oxo-Clusters at Interfaces

J.F. Gérard<sup>a</sup> and L. Dai<sup>b</sup>

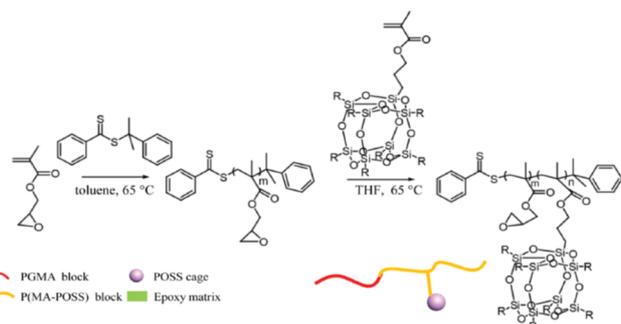
<sup>a</sup>Ingenierie des Matériaux Polymères UMR CNRS 5223 - Université de Lyon / INSA Lyon, Villeurbanne, France

<sup>b</sup>College of Materials Science - Xiamen University, Xiamen, China

### Abstract

Metal-oxo clusters such as polyoligomeric silsesquioxanes could be considered as well-defined nano-building blocks to design inorganic-organic nanostructures in polymers. The inorganic character of the core and the nature of the ligands and reactive groups allows to copolymerize them with various monomers to prepare random copolymers, block copolymers, and polymer networks. In such a way, block copolymers were synthesized by reversible addition-fragmentation chain transfer controlled radical polymerization of methacrylate monofunctional POSS and MMA or styrene or butyl acrylate (1). Depending on the nature of the ligands, different types of nanostructures could be generated from self-assembling process, i.e. microphase separation between the POSS blocks and the organic ones. The nanostructures issued from the POSS clusters assembling could introduce or combine functionalities such as optical and thermal properties and allow the formation of templates.

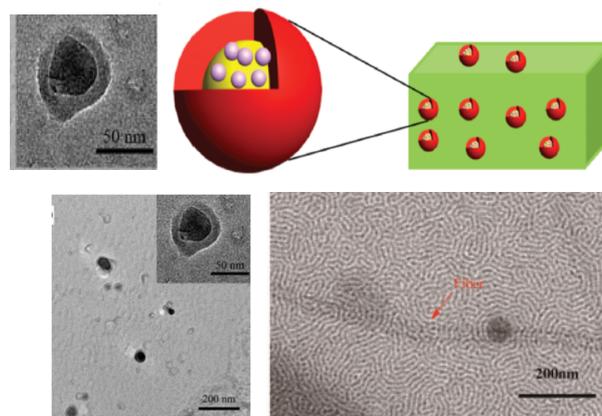
In a previous work (2), poly(methyl methacrylate-*b*-POSS methacrylate) BCP were synthesized by RAFT and introduced as modifiers in epoxy-amine reactive systems. In fact, the PMMA block is miscible in such systems whatever the conversion and allowed the formation of micelles having assembled POSS core. In this case, a similar concept was used. The lecture will illustrate the design of block copolymers from methacrylate-POSS (MA-POSS) and glycidyl methacrylate (GMA) monomers by RAFT-polymerization (Figure 1). RAFT polymerization was selected as it was demonstrated that the large steric hindrance of the POSS cage with ligands (isobutyl, cyclohexyl, or phenyl) limits the degree of polymerization in atom transfer radical polymerization (ATRP).



**Figure 1.** Synthesis of poly(glycidyl methacrylate-*b*-POSS methacrylate) block copolymer (1).

To obtain novel polyhedral oligomeric silsesquioxane (POSS)-based nanostructures, the copolymerization of methacrylate-POSS (MA-POSS) and glycidyl MA (GMA) was performed via reversible addition-fragmentation chain transfer process. The as-synthesized poly(glycidyl methacrylate) poly(GMA)-*b*-MA POSS) block copolymers (BCPs) were characterized by <sup>1</sup>H NMR spectroscopy,

FT-ir spectroscopy, and size exclusion chromatography (SEC). The introduction of this POSS cluster improved the thermal stability of the BCP. Then, poly(GMA-*b*-MA POSS) copolymer was reactively incorporated into 4,4'-methylene bis(2,6-diethylaniline) based epoxy network. Compared with conventional non-reactive poly(MA-POSS-methylMA) (POSS-MMA) copolymers (15 wt% and 45 wt% POSS, respectively), poly(GMA-*b*-MA POSS) can self-assemble in epoxy reactive thermoset to micelles with diameters of 20–40 nm. Due to the formation of uniform nanostructures, reactive POSS-modified epoxy composites exhibit higher glass transition temperature, *T*<sub>g</sub>, and displays a two-times higher rubbery state modulus than neat epoxy. As a consequence, this work proposes an efficient route to synthesize POSS-based nanocomposite via the introduction of (nano)structurable poly(GMA-*b*-MA POSS) which can pre-react with reactive monomer.



**Figure 2.** (a & b) Formation of nanostructures from poly(glycidyl methacrylate-*b*-POSS methacrylate) block copolymer in the epoxy network (1); (c) Nanostructuring of the neat copolymer poly(glycidyl methacrylate-*b*-POSS methacrylate) block copolymer)

As a consequence, this work offers an efficient route to synthesize POSS-based nanocomposites via the incorporation of block copolymer such as poly(GMA-*b*-MA POSS). Further studies are considered to use similar block copolymers to nanostructure different types of polymers such as polyamides (PA), polyethylene terephthalate (PET), polyurethanes (PU), and polyurethane-acrylates (PUA). From such an approach, new coatings, foams, and polymer composite matrices could be prepared.

### References

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