



# A molecular characterization of hyper-cross-linked hybrid polyPOSS-imide networks



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## ABSTRACT

Hybrid hyper-cross-linked membranes based on inorganic polyhedral oligomeric silsesquioxanes (POSS) covalently bonded with organic imides have been shown to maintain remarkable molecular sieving abilities and gas separation performances up to 300 °C. These films are obtained through the interfacial polycondensation of POSS with a dianhydride, leading to a polyPOSS-(amic acid) network, which is then converted to a polyPOSS-imide network by thermal imidization. Using the pyromellitic (PMDA) dianhydride as a test case, the underlying molecular structures have been generated by molecular dynamics (MD) simulations and specific algorithms which closely mimicked the mixing, polycondensation and imidization steps of the experimental scheme. This allowed realistic models of the final cross-linked imide networks to be compared with their un-cross-linked monomer mixtures and their intermediate amic-acid precursors. Both the formation of the network and the subsequent imidization decreased the density as the systems became sterically more constrained. The volume shrinkage during imidization was less than expected considering the amount of water removal. This led to a larger void space and an improved gas solubility for the polyPOSS-imide films. Although the networks were constructed with the experimentally-found average of four linked arms per POSS, the distribution of the number of links per POSS were quite wide with a range from zero to the maximum possible of eight links per POSS. There was also considerable heterogeneity in the POSS-imide-POSS angles, which was related to the flexible aliphatic linker between the organic and inorganic moieties. Thermomechanical analyses confirmed that these cross-linked materials were well-suited for high-temperature applications. When subjected to uniaxial tension, they strain hardened at large deformations and their elastic moduli remained solid-like at high temperatures.

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## 1. Introduction

Gas separation by nonporous glassy polymeric membranes has long been investigated as an alternative to the more conventional cryogenic distillation or adsorption separation processes because of the smaller sizes of the membrane devices and their lower energy costs. Their main applications include the separation of common gases such as O<sub>2</sub>, N<sub>2</sub>, He, H<sub>2</sub>, CH<sub>4</sub> or CO<sub>2</sub> from air, natural gas, flue gas, syngas or other petrochemical products [1,2]. Many gas permeabilities and selectivities of polymer membranes have been reported in the literature [2,3], but most of them were measured at 25–35 °C. On the other hand, some industrial applications

such as the treatment of syngas directly from the water gas shift reactor or the treatment of power plant flue gas involve processes at much higher temperatures [4].

There are only very few polymers, among which polyimides [5] and their thermally-rearranged derivatives [6,7], which are able to maintain gas molecular sieving abilities at temperatures of 200–300 °C. High-performance polymers can also be crosslinked, which suppresses plasticization and improves resistance [8]. However, inorganic materials usually exhibit even better thermomechanical properties. As such, hybrid materials based on both organic and inorganic moieties have gained attention for potentially combining good gas separation properties along with thermomechanical resistances and cost-efficiencies [9]. These so-called hybrid organic-inorganic membranes include both the blends in which the inorganic phases are physically dispersed in the organic matrices [10], as well as the networks in which the inorganic and

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organic components are linked through strong ionic or covalent bonding [11].

Polyhedral oligomeric silsesquioxanes (POSS) [12], with the basic formula  $(\text{RSiO}_{3/2})_n$ , are one of the emerging classes of hybrid organic–inorganic materials for controlled gas transport properties [13]. They are based on rigid inorganic siloxane cages functionalized with flexible organic substituents R at their corners. There are many different POSS depending on the nature of R and the value of  $n$ , which typically varies from 6 to 16 [14]. However, the most extensively studied up to date are the cubic POSS with  $n = 8$ , i.e.  $\text{Si}_8\text{O}_{12}$  cages functionalized with eight pendant organic arms [12]. Within the context of permeation, small gas molecules can move through the intertwined organic chains [13], but POSS are rarely studied on their own since their membrane-forming capacities are limited. On the other hand, gas transport properties have been investigated for polymeric membranes that use either POSS as physical fillers or covalently bonded with organic moieties of various lengths [9,15–18]. In both types of materials, these hybrid membranes can include oligo- or polyimides as the organic component [19–22]. Poly(imide silsesquioxane)s also find applications in other high-performance domains [23], such as fuel cells [24,25] or space survivability [26].

Recently, Raaijmakers, Benes and coworkers have developed a method for the facile production of ultrathin and hyper-cross-linked films consisting of networks of POSS covalently bound with organic imide moieties [27–30]. This approach is based [31] on the polycondensation of a primary amine-functionalized POSS with a dianhydride at the interface between two immiscible solvents, which results in the formation of an homogeneous polyPOSS-(amic acid) film. The amic acid groups are then converted into cyclic imide groups via thermal imidization at temperatures up to 300 °C, thus producing a defect-free polyPOSS-imide thin film. This method has been applied to various dianhydride linkers and shown to lead to hyper-cross-linked networks with tailored molecular sieving capabilities, which are able to maintain gas separation performances up to 300 °C. In addition, the facile synthesis conditions and the defect-free processability are well adapted to large-scale production [27–30].

The high thermal stabilities of those polyPOSS-imides have been attributed to the hyper-cross-linked nature of the thin films. It has been shown using X-ray photoelectron spectroscopy (XPS) that on average, four out of the eight functional groups on each POSS react with a dianhydride, the four remaining groups mainly consist of amines, and both anhydride groups on each dianhydride are converted to cyclic imide bonds [27,28,30]. However, it is unclear how the actual linkages are distributed within the material at the molecular level. The present work thus attempts to bridge the gap between the experimental characterizations and the underlying molecular structures by using molecular dynamics (MD) simulations and construction algorithms which closely mimic the entire experimental reaction scheme. The pyromellitic (PMDA) dianhydride is chosen here as a test case. Molecular models of amino-functionalized POSS and PMDA dianhydrides are first prepared separately at room temperature and then put into contact to represent the initial conditions for interfacial polycondensation. Several algorithms are tested to carry out the actual polycondensation reaction and create the intermediate polyPOSS-(amic acid) networks. The models are then heated up and subjected to an algorithm which converts the amic groups into cyclic imide groups, thus creating the final model polyPOSS-imides films.

Molecular models of cross-linked materials are usually based on heuristic distance criteria with various relaxation procedures [32]. Essentially two approaches have been used to create networks from atomistic models of the mixtures of the reacting molecules, most of them related to epoxy-based thermosets [33–44]: (i) formation of the entire network from a single static configuration

and (ii) progressive formation of the network via alternating reaction and relaxation cycles. In the first case, the problem is essentially equivalent to solving the travelling salesman problem for which solutions exist, e.g. the simulated annealing technique [36,38]. The static approach inevitably leads to longer and longer initial bonds being defined as the degree of cross-linking is increased and considerable strain can end up being trapped in the resulting structures [33]. Progressive formation of the network can in part alleviate this problem as strains induced by creating long bonds are relaxed out. For example, it is possible to link a pair of sites at each reaction step before carrying out cycles of energy minimization and MD to shrink the newly created long bond and re-equilibrate the system [34]. Such a one-by-one approach is not entirely satisfactory in that the time required depends on the system size. Heine et al. [45] proposed a dynamic cross-linking method for poly(dimethylsiloxane) networks, where all reacting sites within a pre-specified range at each time step reacted in the course of an MD simulation with specific bonding potentials for the newly created bonds preventing instabilities developing in the dynamics. Varshney et al. [35] coupled the dynamic cross-linking concept with the iterative cycles of energy minimization and MD, along with a multistep relaxation procedure based on variable bonding force constants and distance criteria. Although there were differences in the details (for example the chosen cutoff for cross-linking), similar bond-forming/relaxation approaches have been applied successfully both to epoxies [36–38,41] and to other networks [46–48]. Several aspects have been further explored, such as the evolution of the partial atomic charges during curing [39], the formation of bonds being based on reaction kinetics instead of a distance criterion [40], or the use of a modified Lennard–Jones instead of a bond potential [42].

Coarse-graining approaches have also been used to create networks [36], most of the reported work dealing once again with epoxies [49–51]. These typically involve mapping the reaction mixture to a coarse-grained (CG) system, performing the network-forming reactions in the CG system and back-mapping to an atomistic model [49]. However, the mapping/reverse mapping procedures are far from being straightforward [52] and such elaborate approaches are mostly pertinent if the reaction rates become too slow in the atomistic system or if the diffusion of the reactants is important, e.g. through the formation of density gradients [50,51]. This is not necessary here as the POSS + PMDA mixtures are already solid-like and their reaction rates are known to be relatively fast: the resulting membranes are thin [27,29,30], i.e. the formation of the network is rapid with respect to the diffusion of the reacting species through the forming membrane. Finally, rather than starting from a monomer mixture, it is also possible in both fully-atomistic and coarse-grained approaches to construct polymer chains in a first step and cross-link them in a second step, either directly or by adding linkers. This has been done for networks based on e.g. polyamide [32], polystyrene [53], polydimethylsiloxane [54] or liquid crystalline elastomers [55].

In the present case, we use a similar generic approach as the fully-atomistic bond-forming/relaxation procedure and apply it to the specific hyper-cross-linked POSS-imides under study. While some of the aforementioned simulations do include POSS moieties (usually at fairly low loadings) [36,38,47,48,54], the linkages based on single dianhydride moieties are hereby much shorter, thus leading to closer POSS · · · POSS distances. In addition, the novelty is that the cross-linking intermediate, the polyPOSS-(amic acid) form, is specifically simulated before being transformed into the final polyPOSS-imide form. The model networks are thus created in a way as close as possible to the experimental films and some input parameters, such as the stoichiometry and the degree of cross-linking, are provided by the experimental conditions.

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