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**Synthesis of a Silsesquioxane Based Supramolecular Polymer**

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Honors Project

Submitted to the University Honors Program at Bowling Green State University in partial fulfillment of the requirements for graduation with University Honors

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## **Abstract**

Research toward smart materials, specifically self-healing polymers, is an expanding topic within the materials science field. These materials rely heavily on dynamic crosslinking that is achieved by inducing different degrees of hydrogen bonding, van der Waals forces, etc. This work, demonstrated by research previously done within the Ostrowski research group, shows how coordination bonds of transition metals have been shown to create light activated, self-healing properties. Work done with these light-activated chromium (III) complexes with a poly(butylene-co-ethylene) backbone have shown how metal—ligand coordination geometries can tune mechanical properties of the polymeric material. However, these materials suffer from being incredibly soft and gel like and lack mechanical strength needed for durable coatings. A collaboration with the Furgal lab aims to make the mechanical and thermal properties of the previously synthesized polymer more applicable through the addition of silsesquioxane and siloxane structures into the polymer matrix, which offer thermal stabilities greater than 300 °C and a tunable modulus. These silicon based compounds will be used as composites (through mixtures) and/or covalently attached to increase the cross-link density, inherent stability and spatial alignment of the previously synthesized metallosupramolecular polymer matrix. The final polymer-silsesquioxane product is hypothesized to have a more rigid and applicable structure for advanced coatings while maintaining or enhancing the optical properties of the polymer.

## **Introduction**

Research for self-healing polymers is an expanding topic within the material science field. Self-healing materials are referred to as “smart materials” where they are defined by their ability to significantly change in a controlled fashion through various stimuli.<sup>1</sup> Examples of smart materials include self-healing or shape retaining materials through the use of temperature, pH, moisture, stress, or light stimuli.<sup>1</sup> These synthetic materials can be designed to interact with multiple different stimuli and therefore allow for a wider range of applications.<sup>2</sup> In nature, this self-healing is prevalent at both the micro and macro scale; ranging from DNA repair to healing broken bones.<sup>3</sup> These examples seem rather trivial because of how often they are seen in nature, however, recreating nature's abilities through chemically created materials is quite challenging. A part of the challenge is nature's ability to work based on a “damage prevention” system, while these chemically created materials follow more of a “damage management” route.<sup>3</sup> For this reason,

there have been an increase in proposed strategies to recreate these nature based, stimuli responsive systems.

These material systems are made possible through their heavy dependence on dynamic covalent bonding within the polymer network.<sup>4</sup> This covalent bonding and further achieved crosslinking is made possible by including different degrees of hydrogen bonding, van der Waals forces, etc. By changing the dynamic connectivity of these materials, properties that would normally be unattainable with permanently crosslinked materials can be achieved.<sup>4</sup> Previous approaches to create self-healing polymer matrices have included using channels for contents to flow through the cracks, polymerize, and bridge the flawed areas,<sup>5-7</sup> or possibilities for bond rearrangement<sup>8-10</sup>. Incorporation of dynamic covalent bonds within the backbone of the polymer network is crucial for bond rearrangement, whereas exchange and reorganization for self-healing approaches proceed through reversible chemical reactions.<sup>4</sup> Approaches that include reversible chemical reactions can also be seen with shape retention in hydrogels through oxidative and electrochemical stimulation made possible by the addition of copper.<sup>2</sup> Adding metal to the polymer networks has shown to create a two part system. A stable, covalent system that maintains the shape and a dynamic system induced by the metal coordination between the metal and the side groups of the polymer.<sup>2</sup>

Metal coordination crosslinked polymer networks were first demonstrated by Belfiore et al. where they added various metal salts to a polymer and caused multiple mechanical property changes to the polymer.<sup>11</sup> Further studies since then have shown that metal coordination complexes when placed in or on the backbone of the polymer can also be used to crosslink gels<sup>12</sup> and rubbers.<sup>13</sup> The use of metal coordination complexes allows for a greater range of possibilities and control when designing a polymer network.<sup>14,15</sup> It is also seen that supramolecular polymers that are assembled from low molecular weight monomers by non-covalent interactions, such as metal coordination, have shown traditional polymeric properties. These properties are an important resource in the development of stimuli-responsive dynamic materials.<sup>16</sup>

This knowledge and increased control on designing complex systems has led to recent research to create self-healing polymers through coordination complexation. Depending on the transition metal and oxidative state, different coordination complexation can be achieved and inherently different mechanical properties of the polymer. Through the use of chromium coordination bonds, a self-healing, dynamic crosslinked polymer with photochemical properties

was established by the Ostrowski Lab at Bowling Green State University. The study showed that mechanical properties of polymer matrix could be tuned depending on the choice of ligand. A metallosupramolecular polymer of a poly(butylene-co-ethylene) backbone and attached ligand groups that varied in bonds to the polymer were synthesized to justify this conclusion. Figure 1 displays the polymers with increasing amount of attachment between the ligand and the polymer linker used in the study.

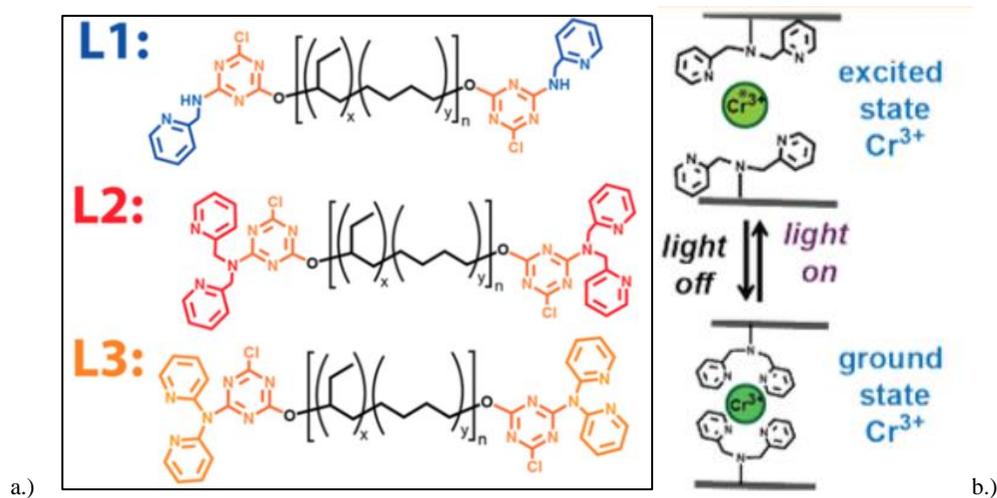


Figure 1: Three polymer and ligand groups (L1-L3) used when synthesizing metallosupramolecular polymer. The center black portion of the structures is the polymer, the orange cyclic structure outside on either side of the polymer is the linker. Through this work, it was concluded that differing degrees of substitution between the linker to the ligand resulted in differing mechanical properties. Further concluding that the ability to tune mechanical properties through ligand choice. 1b) Mechanism of Cr(III) coordination and dissociation with light.<sup>1</sup>

It was shown that the lack of carbon bonds between the nitrogen of the linker and the carbon of the ligand caused there to be an increase in rigidity. Inversely, the more carbon bonds between the nitrogen and the ligand ring causes increased flexibility of the polymer. In addition, it was found that the polymers that contained chromium (III) ions coordinating showed photo responsive behavior due to the Cr(III) ligand bonds (Figure 1b).<sup>17</sup> When 450 nm light is applied to the Cr(III) coordination sites, the ligands are released, and upon relaxation reform bonds.<sup>17</sup> Due to this photochemistry, this polymer provides a promising future within the self-healing coating application industry. Further work with these materials includes enhancing the mechanical strength to be less soft and gel like such that durable coatings can be created.

As described, the ideal structure of a self-healing material includes that the polymer must be hard enough that it retains shape and the bonds can be broken by stimuli, but soft enough that the bonds will be able to freely move and reconnect upon stimuli. A collaboration between the Furgal and Ostrowski labs at Bowling Green State University aims to promote this ideal structure

and make the mechanical and thermal properties of the previously synthesized polymers (L1 and L2, Figure 1) more applicable through the addition of silsesquioxane and siloxane structures into the polymer matrix. Silsesquioxanes are organosilicon compounds that form cage-like structures. The generic structure of a silsesquioxane is shown in Figure 2. These organosilicon compounds are considered a hybrid of inorganic and organic chemical means due to their inner inorganic frame work being made up of silicon and oxygen while the external area of the cage is covered in organic substituents.<sup>17</sup> These substituents, as denoted in Figure 2, can be taken as a multitude of different groups. In previous studies, it has been shown that using mixed R groups can form cages with both or all functional groups present.<sup>20,21,22</sup> By using a mixture of functional groups instead of only the polymer to place on the cage can be beneficial when trying to achieve appropriate mechanical properties.

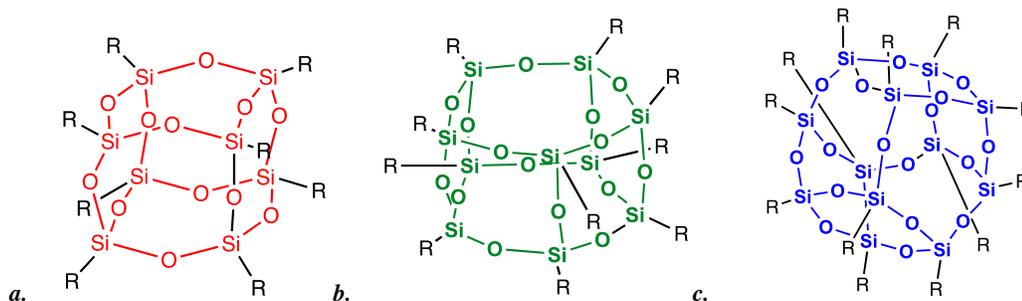


Figure 2: Generic structure of a silsesquioxane molecule containing both inorganic (silicon and oxygen backbone) and organic R-group components.<sup>19</sup> 1a) 8 sided SQ cage structure (T8) 1b) 10 sided SQ cage structure (T10). 1c) 12 sided SQ cage structure (T12). For all structures, R= H, Me, vinyl, etc.

Unlike many silicones, silica, or fillers, the silsesquioxane molecule contains enough organic substituents on its surface to make the molecule compatible with many polymers, biological systems, and surfaces.<sup>20</sup> Silsesquioxanes in the T8 (Figure 2 a) anion form do not react with alkyl halides, anhydrides, or groups that are usually reactive towards nucleophilic attack. Therefore, silylation is the only known method to functionalize this silsesquioxane structure.<sup>20</sup> Further, silsesquioxanes can be synthesized with specific functional groups that would allow for nucleophilic substitution on each corner.<sup>24</sup>

Thermal stability, in addition to the increased chemical and oxidative resistance, surface hardening, and mechanical properties<sup>16</sup> makes silsesquioxanes a promising solution to the application difficulties that previously made self-healing polymer faces. By adding the highly

symmetric cage structure, a well ordered 3-D network can be designed to promote crosslinking and rigidity necessary for durable coating applications.

## Results and Discussion

The initial process to incorporate silsesquioxanes into the original polymer matrix (L1 and L2, Figure 1) was to directly attach the polymer backbone to each cage corner. The metallocupramolecular polymers would be functionalized with a vinyl group using nucleophilic substitution on the last remaining chloride on each end of the triazine structure, or by using two sets of poly(butylene-co-ethylene) polymers, one functionalized with the cage and the other functionalized with metal coordination sites (Figure 3). The vinyl group introduced in these structures can be used to attach the silsesquioxane cage by a hydrosilylation reaction, which couples the Si-H bond to any double bond through a catalytic process.

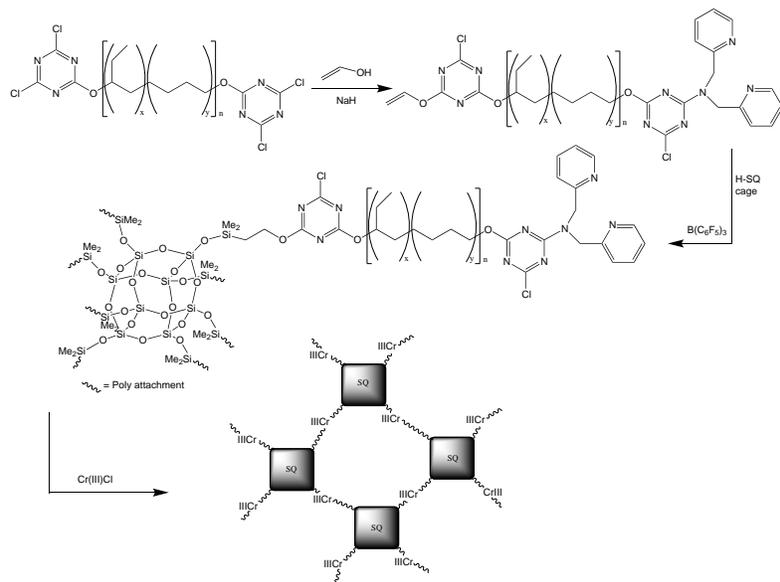


Figure 3: Example Synthesis of silsesquioxane (SQ) containing metallocupramolecular polymer.

By using this synthetic route, a 3-D polymer network of cages connected by poly(butylene-co-ethylene) backbone and chromium coordination could be created. The problem with creating this system is the lack of selectivity when functionalizing the poly(butylene-co-ethylene) backbone with a vinyl group on one side and the ligand group on the other. The resulting product would be a racemic mixture of polymer terminated with both vinyl groups, both ligand groups, or one of each. This mixture would be very difficult to separate into its respective products with no indication of being successful. While this proposed synthetic scheme was unable to be used, it gave inspiration for future reaction schemes.

Because functionalizing the polymer backbone was theorized to be time consuming and ineffective, composites of with L1 and L2 polymers and varying silsesquioxane structures were created. Composites are materials that have two or more materials with differing physical properties, such that when combined they create a material with different properties than the individual components. The individual components are separate from one another and are not bonded together within the finished material. Initially, crosslinkers were created to use in between the silsesquioxane structures. Figure 4 includes the synthetic scheme for diethylene glycol based crosslinking polymers. Polymers with hydride and vinyl terminated functionalization were created so that both a vinyl and a hydride functionalized silsesquioxane cage could be used. The reaction scheme in Figure 4 was used for both the hydride and vinyl terminated diethylene glycol derivative polymers.

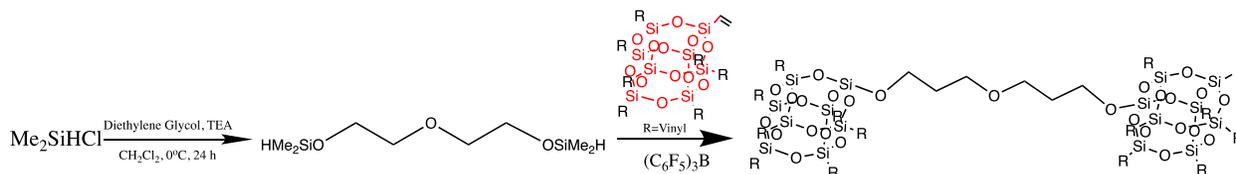


Figure 4: a.) Scheme proposed for functionalizing diethylene glycol and later reacting the "-OSiMe2H" terminated diethylene glycol with the vinylsilsesquioxane structure to create an ethylene glycol silsesquioxane based polymer.<sup>23</sup>

After synthesizing both the hydride and vinyl terminated diethylene glycol derivative polymers, it was hypothesized that the shorter length of the crosslinkers would not be able to soften the overpowering rigidity of the silsesquioxane structure. To combat this, an attempt to combine the two diethylene glycol derivatives was made. This combined polymer structure (Figure 5) has not been reported in the literature and tri(pentafluorophenyl)borane as a catalyst initially.

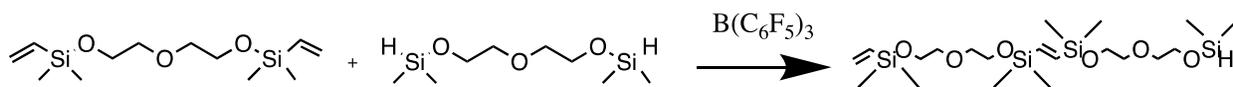


Figure 5: Reaction scheme for the combining the hydride and vinyl terminated, diethylene glycol crosslinkers to create a new

Multiple attempts at combining the polymers were made, however, based on gel permeated chromatography (GPC) each trial was shown to be unreacted. GPC is a size exclusion chromatography method that separates out a sample by molecular weight; with the higher molecular weight components coming out first and those of lower molecular weight coming out last. A successful reaction will yield a GPC spectrum with one broad peak and an unsuccessful GPC spectrum has multiple peaks of the unreacted reagents. Further, nickel bromide was used as the catalyst crosslink the silsesquioxane structures in Figure 4 and to combine the hydride and vinyl derivatives in Figure 5. Nickel bromide was also found to be ineffective in making the

polymers crosslink and combine. Therefore, due to catalytic struggles and time constraints, the project of creating a new crosslinker had to be abandoned. Instead, composites were made using the L1 and L2 polymers with varying ratios (10-30%) of T10 silsesquioxane cages that were functionalized with phenyl groups. Both L1 and L2 based composites were made and Figure 6 is the general scheme for making the composites.

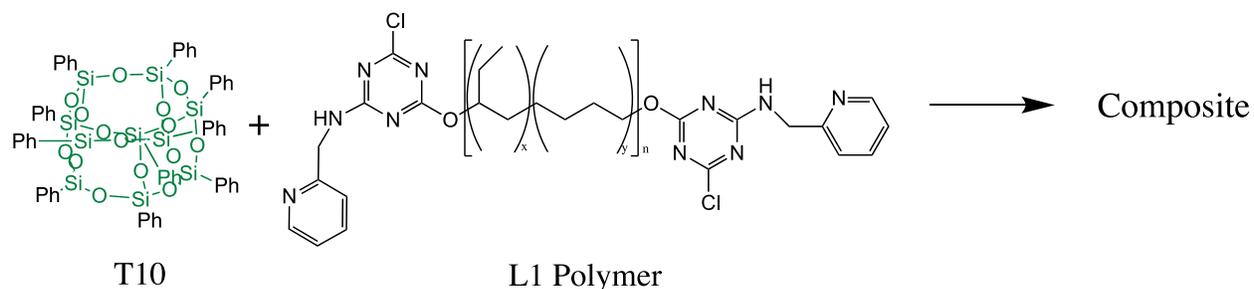


Figure 6: Scheme for creating composites of the phenyl functionalized T10 silsesquioxane and the L1 polymer.

Both sets of composites were complexed in a chloroform and methanol solution, casted into Teflon molds, air dried for one day, and then oven dried for another day. When trying to remove the composites from the molds, it was found that regardless of the amount of T10, all composites were too sticky to be removed and analyzed. Figure 6 is a compilation of photographs taken of the composites from the initial cast time to twenty-four hours later. As the weight percent of T10 was increased, the stickiness of the composite slightly decreased but the amount of imperfections on the surface and separation within the composite increased.

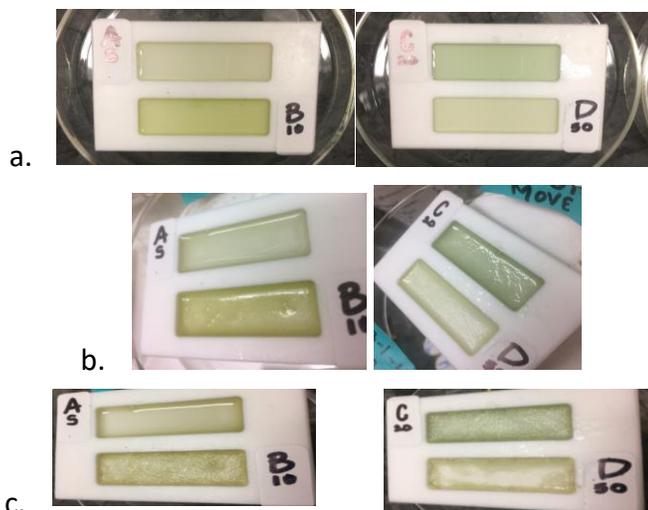


Figure 7: Composites range from A-D with varying percentage of T10 in the composite. A – 10%, B – 15%, C – 20% and D – 30%.  
a.) Time zero - no particles or bubbles forming and A-D are all liquid. b.) 20 minutes of air drying – top of cast is “solid” and bubbles are stuck trying to escape from the lower liquid layer. B-D have courser surface due to slow drying and T10 separating out. c.) 24 hours of air drying - B, C, and D have increased separation. Composites are sticky and stretch easily like very viscus liquids.

Drying the composites has shown to require a more complex procedure than simply air drying as the paper originally suggested. The polymer is soluble in chloroform, hexanes, and low boiling point solvents, therefore, all reactions concerning the L1 and L2 polymer have been done in chloroform. This complicates drying the composites because chloroform evaporates too quickly, leaving the top layer solid-like while the lower layer is fluid. This might not be a problem if it were only one part, however, because it is a two-part system, the T10 structures aggregate together in the bottom, fluid layer instead of creating a well dispersed composite. This is can be seen in Figure 7 (c.) composite D as there is a large amount of separation. A solvent that has a higher vapor pressure would allow for the composites to dry slower, therefore holding the two systems in place while it dries. Less aggregation and separation makes for a better composite.

All composites (A-D) in Figure 6 were too sticky and malleable to be removed from the molds or analyzed by the rheometer. The L2 composites were hypothesized to be have complexation with the chromium because of the consistent pale green throughout A-D in contrast to the light brown color seen in A, B, and D of the L1 composites. All of the L2 composites had similar physical properties to the L1 polymer composites and were too sticky to be removed from the mold. Because both sets of composites were unable to be removed for physical property analysis, it was concluded that the polymer itself is just too sticky for applicable purposes and that another approach would be necessary moving forward.

### **Future and Current Work**

It was hypothesized that changing the backbone of the polymer in length or changing the composition entirely would do little to change the malleability of the polymer as a whole. This left manipulating the silsesquioxane structure as our outlet for further study. Present work aims at attaching a L2 ligand group (Figure 1) to a silsesquioxane cage to coordinate with the L2 polymer such that the physical properties of the polymer network will be altered and become more rigid. Because the coordination of chromium between the silsesquioxane and the polymer will be the same as previously studied since the ligand is remaining the same, the photochemistry and coordination chemistry should remain the same even though it is between two different compounds. The difference in this system will be due to adding the silsesquioxane directly into the polymer matrix and creating a three-dimensional network. Because of this, it is hypothesized the mechanical properties of the polymer network will drastically change and be better suited for

coating application. Figure 7 is the reaction scheme for creating a silsesquioxane cage capable of doing nucleophilic reactions and includes the proposed structure of the final polymer matrix.

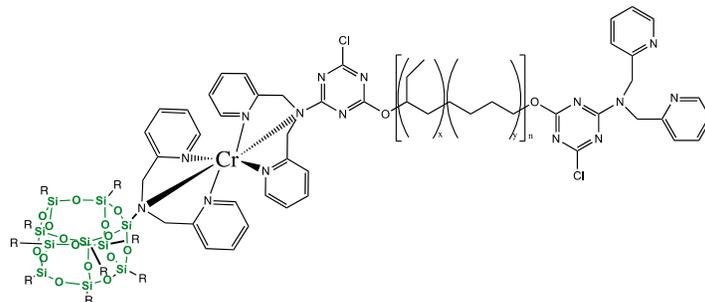


Figure 8: The proposed structure of the L2 and silsesquioxane based, chromium coordinated network. R groups denote L2 ligands allowing for coordination with other L2 polymers or other silsesquioxane structures. The other end of the L2 polymer can be coordinated to another L2 polymer as well as a silsesquioxane.

Two different starting materials will be used to create silsesquioxane structures that will later allow for nucleophilic attack by the L2 ligand groups. Figure 9 denotes two synthetic routes by using (chloromethyl)triethoxysilane and (3-iodopropyl)trimethoxysilane to create chloride and iodopropyl functionalized cages.

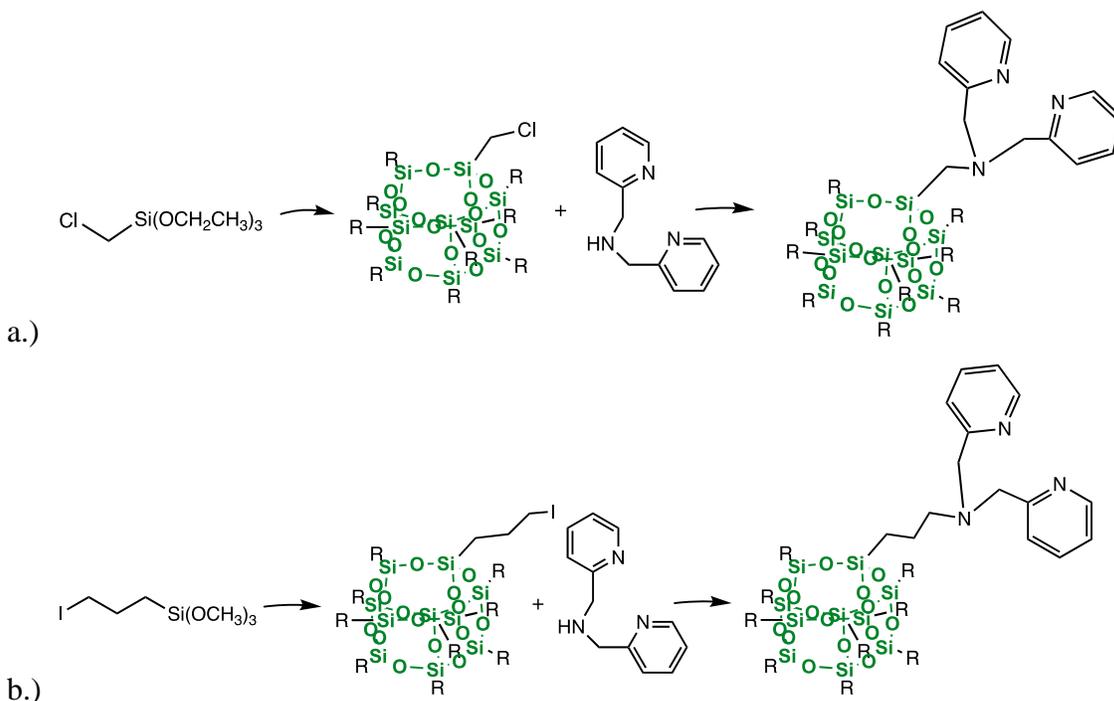


Figure 9: a.) Reaction scheme for creating a silsesquioxane with chloride functionalization. This product will undergo nucleophilic substitution with the 2-picolyamine (L2 ligand) to create the desired 2-picolyamine functionalized silsesquioxane. b.) The reaction scheme for creating a silsesquioxane with 3-iodopropyltriethoxysilane to yield a cage with more space between the silsesquioxane and the L2 ligand. R groups denote functionalization on each corner with the specifically drawn group.

The benefit in creating both the iodopropyl and the chloromethyl cages is apparent in how much space, i.e. how many carbons are in between the silsesquioxane and the ligand group. Because the

silsesquioxane is binding to the chromium and thus the polymer, there is a chance that an overly rigid system will be created if all ten active sites of the T10 silsesquioxane are functionalized. With the polymer being too sticky and malleable to use, the chloromethyl cage that has less space between the cage and ligand group has been hypothesized to enhance the structural stability significantly. However, using the chloromethyl cage may yield to an overly rigid polymer matrix in comparison to that of the iodopropyl cage that has two more carbon bonds between the silsesquioxane and ligand group. Therefore, if the chloromethyl cage is in fact too rigid, using the iodopropyl cage could be ideal to create an applicable polymer matrix. Testing these functionalized cages can also teach about fundamental mechanical properties of silsesquioxanes and how they relate to their substituents.

### **Conclusions**

The previously synthesized self-healing polymers lacked mechanical properties that are desirable for coating application. Different schemes to incorporate the silsesquioxane structures were attempted that incorporated little change to the L1 and L2 polymer backbone, one attempt included creating composites. The composites were made of L1 and L2 polymer with varying percentages of T10 phenyl silsesquioxane structures and were coordinated with chromium. All composites, regardless of T10 percentage, were concluded to be too soft and sticky for property testing. Future attempts will include creating a silsesquioxane structure that is able to do nucleophilic substitution with the L1 and L2 polymer ligands. This reaction scheme is hypothesized to create a more rigid polymer matrix by inducting the silsesquioxane directly into the polymer matrix.

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