Experiment #5 – Bouncy Balls

Introduction

Organopolysiloxanes are polymeric materials containing silicone, oxygen, and organic groups. Methylsilicones (also called dimethylpolysiloxanes) are the most important members of this class of materials. The term "silicone" was first used to describe chemicals that had an empirical formula of R_2SiO. Although ketones, $R_2C{=}O$, exhibit a similar structural motif to silicones, silicones bear little resemblance to ketones. Carbon shows a strong tendency to form π bonds, and ketones have the structure RR'C=O, with a double bond between the carbon and oxygen. They are generally simple molecular compounds. Silicon, on the other hand, does not show this tendency, and double bonds between silicon and itself or other elements are relatively unstable. Silicon, unlike carbon, possesses empty, low energy *d* orbitals, which can effectively overlap with filled π orbitals on other elements, such as nitrogen, oxygen, or fluorine. This fact results in unusually short bond lengths and stable single bonds.

Organopolysiloxanes are prepared by the hydrolysis of the selected chlorosilanes, generating $(CH_3)_2Si(OH)_2$, followed by condensation of the resulting silanols (Figure 2.3). The generated polysiloxanes are a mixture of cyclic compounds (where n = 3 4, 5, etc.) and open chain compounds with hydroxyl end groups. The cyclic compound (most often a tetramer) is then polymerized to the linear polymer through the use of heat or a catalyst under acidic or basic conditions. The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$, a monofunctional compound called an endblocker, to the reaction mixture. The absence of an endblocker can produce chains of high molecular weight, which are referred to as silicone gums.

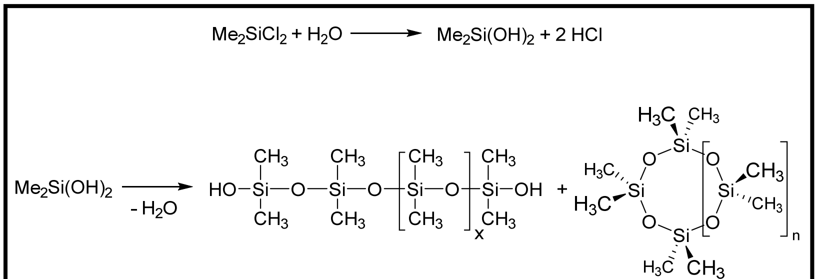

Figure 5.1. Generation of silicone polymers from the hydrolysis of Me_2SiCl_2.

Silicone polymers have a wide range of viscosities, lubricating properties, and reactivities. These polymers are widely used in industrial chemistry in automobile polishes, cosmetics, water repellants, high-temperature electrical insulation, gaskets, release agents, antifoam agents, high-temperature paints, glass cloth laminates, elastomers (rubbers), greases, and other general polymers. The framework of all the polymers is the very stable -Si-O-Si- sequence, which gives silicones good thermal stability at high temperatures (above 500 °F) as well as flexibility at low temperatures (below -110 °F). The organic groups are hydrophobic, and thus, so is the polymer. Medical grade silicones are used widely in areas such as silicone rubber finger joints for those suffering from arthritis, mammary implants following radical mastectomy, hypodermic needles lubricated with silicone fluids to make insertion reasonably painless, and silicone rubber coatings encasing implants such as pacemakers and infusion pumps to name a few.

In this experiment, the chemistry of silicones will be investigated by preparing a silicone polymer, via the hydrolysis of dichlorodimethylsilane (completed for students prior to the chemical Olympiad). The silicone, containing residual hydroxyl groups will be cross-linked using boric acid. This trifunctional acid, $B(OH)_3$, which also contains hydroxyl groups, forms -Si-0-B- linkages resulting in a gum like material.

A cross-linker is a type of molecule that attaches to other molecules in either covalent or ionic bonds. In this case, boric acid is the cross-linker and the amount of cross-linker added is important towards giving the physical properties of the overall bouncy ball. Shown in Figure 5.2 is the graphical representation of the addition of more and more $B(OH)_3$ cross-linker to a PDMS polymer. In this experiment you will be choosing the concentration of cross-linker to add to your ball to get the highest bounce.

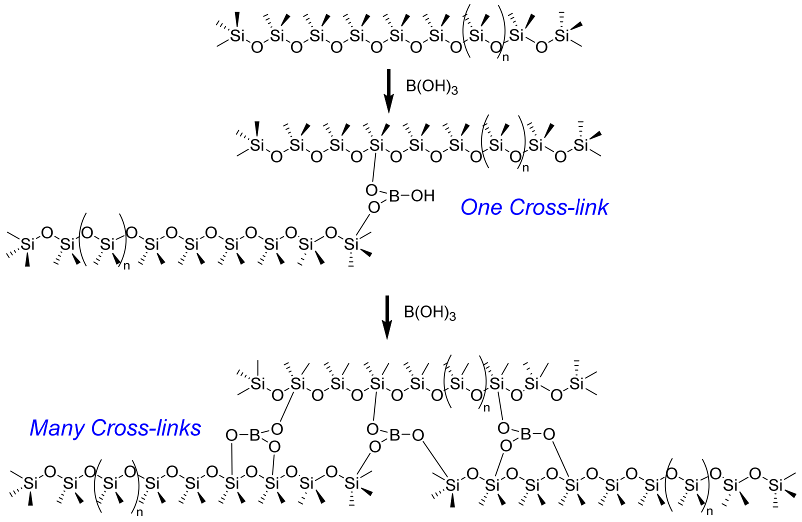

Figure 5.2. Graphic of Cross-linking of PDMS with boric acid.

Another way to look at cross-linking polymer networks is that they can provide a 3D structure and bulk physical properties vs. the chemical properties and chain lengths of the polymer backbones as illustrated in Figure 5.3.

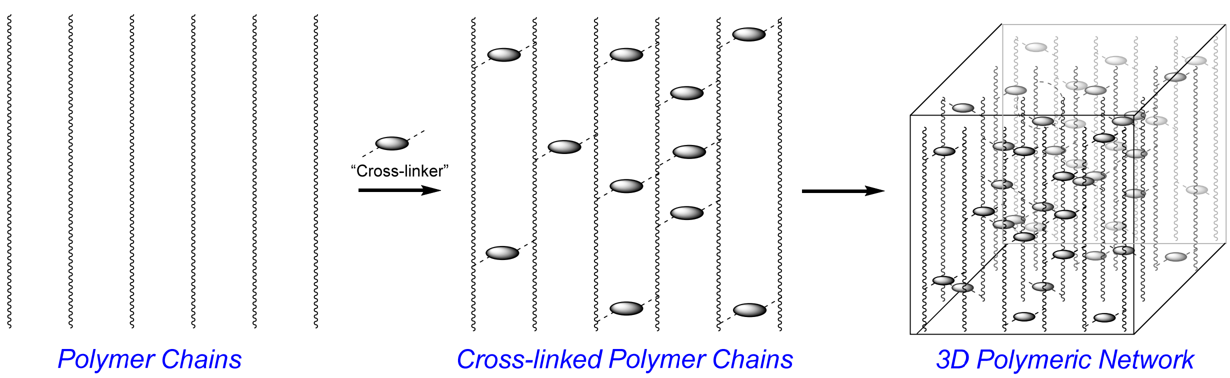

Figure 5.3. Theoretical view of adding cross-linkers to polymers to give rise to a variety of linkages that can alter the 3D physical properties of the resulting material.

Procedure:

Safety Precautions: Dichlorodimethylsilane is harmful if swallowed, inhaled, or absorbed through the skin. It is extremely destructive to mucous membranes as it reacts rapidly with water to release HCl gas.

Step 1 (Completed prior to Chemical Olympiad)

1. Place 30 mL of diethylether into a 250 mL round bottom flask with a stir bar, and 15 mL dichlorodimethylsilane.
2. Cap the flask with a condenser, and **slowly** add 30 mL H_2O through the top of the condenser. Fast addition of water will result in the mixture spraying all over the hood. Allow the mixture to stir for 10 minutes.
3. Remove the water layer with a pipette and discard. Replace the condenser, and slowly add 15 mL 10% sodium bicarbonate solution, stir until bubbles no longer form.
4. Remove the water layer with a pipette and test the pH of the water layer using pH paper. Repeat addition and removal of 10% sodium bicarbonate until the water layer is no longer acidic. Finally, wash the organic layer with 30 mL H_2O and remove the water layer.
5. Run through a 10 mL syringe filled with silica gel (to the 2.5 mL mark) topped with sodium sulfate (to the 3 mL mark). Collect the eluent and wash the column with an additional 45 mL diethylether. Concentrate the solution with slow heating under a stream of nitrogen. Weigh the product.

Step 2 (Completed at Chemical Olympiad)

6. Add the boric acid, the amount (ranging between 1 and 20 wt %), stirring constantly with a spatula to the PDMS obtained from part 1. Heat to 170 – 180 °C until a gum consistency is obtained, around 20 minutes. **Cool to room temperature**.
7. Once cooled, remove the vial from the hot plate and knead the gum (with your gloved fingers) until the silicone polymer resembles a ball.
8. Perform a bounce test with your polymer ball next to a ruler, recording how high the ball bounces. Repeat this experiment three times and report the average value.

Notes:

Weight Percent of Boric Acid	Bounce Height #1 (cm)	Bounce Height #2 (cm)	Bounce Height #3 (cm)

HOW HIGH WAS YOUR HIGHEST BOUNCE? _________________ CM

AVERAGE BOUNCE HEIGHT: _________________ CM

NAME _________________________________ High School __________________________