

EXPERIMENT 1

Silicon Polymers: Preparations of Bouncing Putty (Silly Putty)

REFERENCES

- a. Szafran, Z.; Pike, R. M.; Singh, M. M. *Microscale Inorganic Chemistry*, Wiley, New York, 1991, p. 176

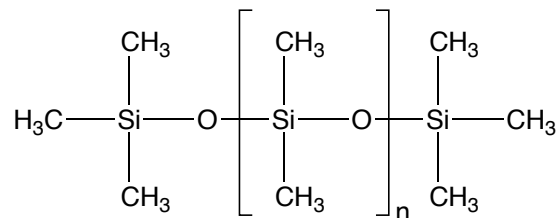
SAFETY RECOMMENDATIONS

Dichlorodimethylsilane ($\text{Si}(\text{CH}_3)_2\text{Cl}_2$) is harmful if swallowed, inhaled or absorbed through the skin. It is extremely destructive to the mucous membranes. The compound reacts violently with water.

Boric Acid ($\text{B}(\text{OH})_3$) is toxic if ingested.

INTRODUCTION

Silicones, or more specifically polyorganosiloxanes, are an interesting class of inorganic polymeric materials that consist of chains of alternating silicon and oxygen atoms, with organic groups bonded to silicon. The methyl silicones, also called polydimethylsiloxanes, are perhaps the most important members of this class of materials. A typical structure of a methyl silicone is the silicone oil shown below:

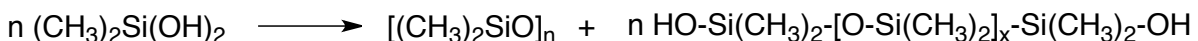
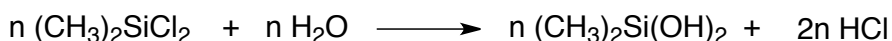


The term “silicone” was first used by Friedrich Woehler in 1857 to describe chemicals that had an empirical formula of “R₂SiO”, in an analogy to organic ketones R₂CO, where R is an organic group. Silicones bear little resemblance to ketones, however, and the differences between these two types of compounds also illustrate a basic difference between silicon and carbon chemistry. Carbon shows a strong tendency to form p 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 pp- pp double bonds between silicon and itself or other elements are relatively unstable, not being discovered until the mid-1980’s.

The most common starting material for the formation of the methyl silicone polymers is dichlorodimethylsilane, (CH₃)₂SiCl₂. This compound is, in turn, made in huge industrial quantities by the action of CH₃Cl on silicon powder in the presence of a copper catalyst at 250- 300 °C (the Rochow Process). The resulting mixture of compounds includes SiCl₄, CH₃SiCl₃, (CH₃)₂SiCl₂, (CH₃)₃SiCl and other less abundant products. The mixture is separated by very careful fractional distillation. Dichlorodimethylsilane is a useful starting material for two reasons:

- (1) The Si-Cl bonds are easily hydrolyzed, making the compound very reactive.
- (2) The compound is bifunctional, since there are two chlorines. The chain can therefore propagate in two directions, resulting in high molecular weight polymers.

The polyorganosiloxanes are prepared by the hydrolysis of the selected chlorosilane. Thus, hydrolysis of (CH₃)₂SiCl₂ gives rise to the corresponding silanol, (CH₃)₂Si(OH)₂ and hydrogen chloride. The outstanding characteristic of the silanols is the ease in which they condense to yield siloxane polymers (compare with alcohols!), as shown in the following reaction sequence:



The polysiloxanes formed are a mixture of cyclic compounds (where $n = 3, 4, 5$, etc.) and open chained compounds having hydroxyl end groups. In the industrial preparation of silicones, the cyclic species are obtained in good yield by carrying the hydrolysis out in dilute ether solution. They are isolated and purified by fractional distillation. The cyclic compound (the trimer and tetramer are most often used) is then polymerized to the linear polymer by a process called **equilibration**. Equilibration of cyclic siloxanes is the process by which the Si-O- linkages are continuously broken and reformed until the system reaches an equilibrium condition at the most thermodynamically stable state. Heat alone or, more commonly, acid or base catalysis is used in the process.

The chain length of the polymer can be controlled by adding $(\text{CH}_3)_3\text{SiCl}$, (an **endblocker**), to the reaction mixture. This compound terminates the chains with an $-\text{OSi}(\text{CH}_3)_3$ group. The absence of an endblocker can produce chains of high molecular weight, often referred to as silicone gums.

Silicones can be prepared having a wide range of viscosities, lubricating properties and reactivities. They see extensive use in industrial chemistry in automobile polishes, cosmetics, water repellants, high-temperature electrical insulation, release agents, gaskets, 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 $-\text{Si}-\text{O}-\text{Si}-$ sequence. This gives silicones good thermal stability at high temperatures (above $269\text{ }^\circ\text{C}$) and flexibility at low temperatures (below $-79\text{ }^\circ\text{C}$; low glass transition temperature T_g). 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 various forms of 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 "bouncing putty", a silicone polymer, via the hydrolysis of dichlorodimethylsilane. The silicone, containing residual hydroxyl groups will be cross-linked using boric acid. This trifunctional acid, $\text{B}(\text{OH})_3$, which also contains hydroxyl groups, forms $-\text{Si}-\text{O}-\text{B}-$ linkages between the siloxane chains, resulting in a peculiar type of gum. The commercial "bouncing putty" found in novelty stores is compounded with softening agents, fillers and coloring agents.

PROCEDURE

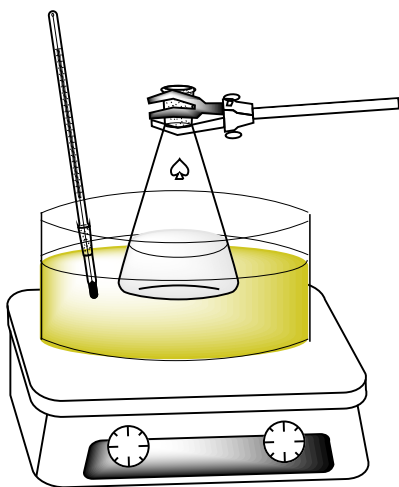
This reaction must be carried out in the fume hood.

Before setting up anything else, put your oil bath on the hot plate and set the temperature as high as possible. The oil needs to reach $\sim 180\text{ }^{\circ}\text{C}$, so add a thermometer in your oil bath and check the temperature regularly.

Wear gloves to place 16 ml of Et_2O in a 50 ml round bottom flask containing a magnetic stirring bar. Using a volumetric syringe add 8 ml of $\text{Si}(\text{CH}_3)_2\text{Cl}_2$ to ether and attach a water condenser to the flask.

Arrange the assembly on a magnetic stirring hot plate and, with rapid stirring, CAREFULLY add 16 ml of water, DROPWISE (otherwise it WILL jump!), through the top of the condenser. (Initially there will be vigorous evolution of HCl gas, and heat generated by the reaction will cause the ether to reflux, hence the need for the water condenser).

Once all the water has been added, allow the mixture to stir for an additional 10 min at room temperature.



Remove the condenser and, using a Pasteur pipette, remove and discard most of the lower aqueous layer. Reattach the condenser and carefully add 8 ml of 10% sodium bicarbonate solution, dropwise through the top of the condenser, with stirring. Evolution of CO_2 gas may be observed as residual HCl in the wet ether solution is neutralized. Once gas evolution has stopped, remove the condenser and, with the pipette used earlier, remove most of the lower aqueous layer. Repeat the procedure with the $\text{Na}(\text{HCO}_3)$ solution

until the lower layer no longer gives an acidic indication (pH paper). Finally, wash the ether solution with 20 ml of water. Separate and discard the aqueous layer.

Transfer the ether solution containing the silicon polymer to a 50 ml Erlenmeyer flask and dry the solution by adding anhydrous sodium sulfate (~ 3 gr). Filter the solution to remove $\text{Na}_2(\text{SO}_4)$, tare a 50 ml Erlenmeyer flask and return the dry ether solution to the flask. **[Good Stopping Point]**

Evaporate the ether, by carefully immersing the flask into the hot oil bath. Once the ether has evaporated, clean the oil off the flask and determine the weight of the clear residual silicone fluid.

Add boric acid to the silicone fluid in an amount of 5% the weight of the fluid, stirring constantly with a spatula. Continue stirring for 5 min.

Heat the resulting mixture to ~ 180 °C in the oil bath with stirring until a stiff silicone gum is obtained (~ 20 min).

Allow the product to cool to RT and roll it into a ball. If the gum is somewhat brittle, continue kneading. (Clean the polymer glassware with MeOH).

Perform and report on the following tests:

- (1) When rolled into a ball, does your product give a lively bounce on a hard surface?
- (2) Does pulling sharply cause the gum to cleave?
- (3) Does pulling slowly result in a stretching reminiscent of chewing gum?
- (4) Does your product flow into a flat plate when placed on a flat surface?
- (5) Is print transferred to the gum when test (4) is conducted on a flat newspaper?