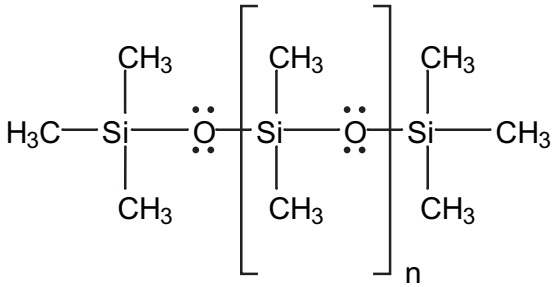
## *EXPERIMENT F*

## SILOXANE CHEMISTRY

### *Preparation of "Bouncing Putty", a Silicone Polymer with Unusual Properties*

Silicones (polyorganosiloxanes) are inorganic polymers that consist of chains of alternating silicon and oxygen atoms with organic groups bonded to silicon. Below is the structure of a methyl silicone, polydimethylsiloxane.




Silicone oil

In this experiment, the chemistry of silicones will be investigated by preparing "bouncing putty", a silicone polymer, via the hydrolysis of dichlorodimethylsilane. This silicone, which contains residual hydroxyl groups, will be cross-linked using boric acid ($B(OH)_3$). This trifunctional acid forms -Si-O-B- linkages resulting in a peculiar type of gum. The commercial "bouncing putty" found in novelty stores is a silicon polymer with softening agents, fillers and coloring agents added.

**Period 1:** This reaction must be carried out in the fume hood.

Wear gloves to measure 20 mL of $Si(CH_3)_2Cl$ (MW = 129.06, density = 1.064 g/mL) in a **dry** graduated cylinder. Rapidly transfer to a **dry** 250 mL Erlenmeyer flask equipped with a rubber stopper. $Si(CH_3)_2Cl_2$ reacts rapidly with moisture to produce HCl gas so make the transfer swiftly. To this add 40 mL of diethylether and hydrolyze by adding 40 mL of $H_2O$ dropwise. HCl gas is evolved in this hydrolysis step. The addition must be made **slowly** at the beginning of the reaction or too vigorous an evolution of the HCl will occur. The ether component will be warmed up to its boiling temperature if $H_2O$ is added too quickly. It is a good idea to have an ice-bath ready to cool down the reaction flask if the hydrolysis becomes too exothermic. The first 10 mL addition of water is very vigorous but less so afterwards. After this initial quantity, you may increase the rate of addition. The product has a very strong odor; be sure to do this in a fumehood!

Separate the ether layer at the completion of the hydrolysis step by pouring the mixture into your 250 mL separatory funnel. Wash the ether layer 3 times with 100 mL (for each wash) of 1 M $Na_2CO_3$. This step is done to neutralize any residual acid remaining in the wet ether solution. Vigorous evolution of $CO_2$ gas is observed at this stage as the neutralization proceeds. Add 10 mL more of diethylether to the flask after the first wash. Finally, perform on additional wash with 100 mL of water. Dry the ether solution over anhydrous magnesium sulfate in a stoppered Erlenmeyer flask, which you may store in your locker.

**Period 2:**

Decant the ether solution, filtering off any magnesium sulfate, into a pre-weighed 50 mL Erlenmeyer flask and evaporate off the ether using a water bath - **not a hot plate**. Note the yield of the dimethylsilicone oil (you should have approximately 9.5 g of material).

Add about 5% (by weight) boric acid (about 0.48 g for a yield of 9.5 g of oil), stirring continuously during the addition and for a few minutes after. This will cause the oil to become very viscous.

Heat the mixture to about 170-180° C in an oil bath and leave at this temperature for 2-3 hours. Allow to cool and remove the product from the flask by scraping it out with a spatula. If the gum is somewhat brittle, continued kneading will produce the desired gum-like characteristic. Once the gum has been removed, clean your Erlenmeyer flask with methanol.

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?

General References


1. J. E. Mark, H. R. Allcock, R. West, **Inorganic Polymers**, Prentice Hall, Chapter 3, 1992.
2. D. F. Shriver, P. W. Atkins, C. H. Langford, **Inorganic Chemistry**, pp. 438-446, 2nd Edn, 1994.
3. F. O. Stark, J. R. Falender, A. P. Wright, **"Silicones"** in **Comprehensive Organometallic Chemistry**, G. Wilkinson, F. G. A. Sone, E. W. Ebel Eds., Pergamon Press, Vol 2, Chapter 9.3, p. 305, 1982.