PREPARATION OF A CROSS-LINKED SILICONE POLYMER

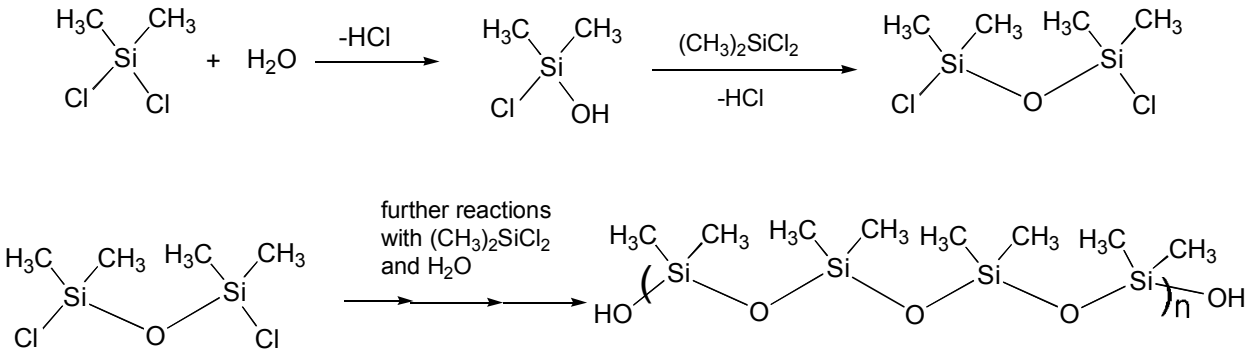
Introduction

This experiment illustrates an industrially important synthetic process, the formation of silicone polymers, and in addition provides some insight into the reactivity of certain types of main-group halides and hydroxy compounds.

The preparation proceeds in two stages: (1) preparation of a polymer from a monomer, and (2) cross-linking of the polymer. The polymer which is initially prepared belongs to a large and important group of polymers called silicones. Silicone polymers all have a $(\text{-Si-O-Si-O-})_n$ backbone, where n is a large number; the two valences of Si not bonded within the polymer backbone are occupied by organic groups such as methyl (CH_3). The formula of the methylated polymer can thus be approximated by $[(CH_3)_2SiO]_n$; its formal name would be poly(dimethylsiloxane). Alkylated silicone polymers are hydrophobic, since the alkyl groups shield the backbone atoms and present an exterior which is for most practical purposes similar to that of an alkane. The backbone, however is important: the type of bond of which it is composed, Si-O, is one of the strongest single bonds known. For this reason, silicones are among the most stable and chemically inert of all polymers.

The physical properties of a polymer can be modified by several different strategies. In the silicone case, one obvious method is modification of the side chains; for instance, hydrogen-bonding groups might be introduced so as to increase the affinity of the polymer for water. Control of the length of the chains is also important: as the chain length increases, the viscosity of the polymer increases. Thus, control of the chain length can be used to make materials which are liquids of various boiling points, greases, waxes, and harder materials (where n is very large). A third method for controlling the properties of a polymer is cross-linking of the polymer chains. The usual result of cross-linking is to increase the hardness and decrease the solubility of the polymer. Other unusual properties can also result, as will be seen in the preparation which you will perform this week.

You will prepare a sample of (poly)dimethylsiloxane, then cross-link the chains by reaction with boric acid. The first step of the process is outlined in the scheme below. The monomer, $(CH_3)_2SiCl_2$, displays the reactivity typical of silyl chlorides: unlike the carbon analogs, compounds with Si-Cl bonds hydrolyze with great ease. The resulting dihydroxysilanes have a strong tendency to eliminate water. This behavior is superficially similar to the behavior of 1,1-diols (ketone hydrates) derived from simple alkyl ketones: loss of a water molecule from one of these molecules generates the ketone.



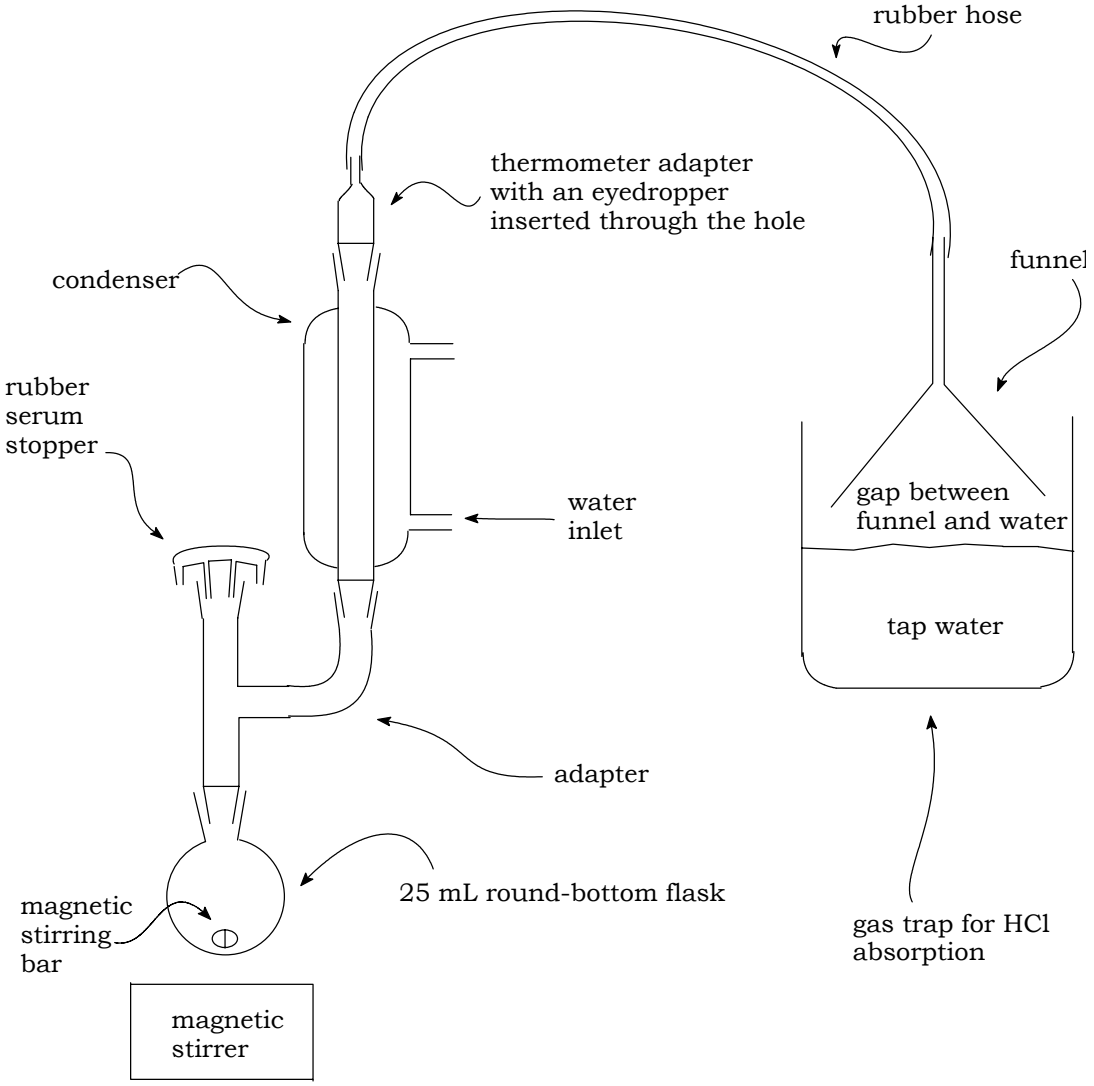
Living Polymer Formation through Hydrolysis of Dichlorodimethylsilane

A similar mechanism of water loss in the silicon case would generate the silicon analog of a ketone, $R_2Si=O$. However, formation of Si=O bonds is highly unfavorable thermodynamically; water is instead eliminated between Si-OH groups on two different molecules to produce a very strong and stable Si-O-Si linkage.

Polymerization of the dihydroxysilanes by intermolecular extrusion of water results in a silicone polymer in which the two ends of the chain contain reactive hydroxy groups. A polymer of this nature, still capable of further reaction or polymerization through the reactive end groups, is called a living polymer. Before a polymer is isolated for processing and conversion to its end use products, the reactive end groups must be eliminated, lest the polymer degrade either by a reversal of the polymerization reaction or by detrimental further reactions of the end groups. Silicone polymers are often end-capped by addition of $(CH_3)_3SiCl$ to the reaction mixture at the end of the polymerization reaction.

In this week's experiment, the ends of the polymer chains will be joined by the use of boric acid, which will yield a cross-linked polymer in which the end groups of the living polymer have been reacted to form Si-O-B linkages. The reaction is an esterification, conceptually analogous to the formation of a carboxylic ester from a carboxylic acid and an alcohol with concomitant loss of water.

APPARATUS FOR PREPARATION OF A SILICONE FLUID



Experimental Procedure[1]

WATCH OUT FOR FLAMES AROUND YOU BEFORE YOU BEGIN.
ETHER IS USED THROUGH MOST OF THE PROCEDURE.

a. Preparation of a Silicone Fluid.

Place 4 mL of diethyl ether in a 25 mL round bottom flask thatcontains a magnetic stirring bar. IN THE HOOD, add 2 mL of dichlorodimethylsilane by use of a syringe.

PLEASE RINSE THE SYRINGE AND NEEDLE THOROUGHLY WITH METHYLENE CHLORIDE SOON AFTER YOU ADD THE DICHLORODIMETHYLSILANE.

Attach an adapter, a water-cooled condenser, a gas trap, and a serum stopper to the flask, as shown in the diagram on the preceding page. Sign the ground-glass-joint items out from the stockroom.

Start the stirrer, then use a new syringe (i.e. not the one which you used for dichlorodimethylsilane) to add 4 mL of water - IN A CAREFUL, DROPWISE MANNER - through the serum stopper to the stirred reaction mixture. Enough heat will be evolved to cause the ether to reflux.

After addition of the last of the water, leave the mixture to stir for an additional 10 minutes.

Use a Pasteur pipet to remove and discard the lower layer of aqueous HCl. Attach the flask to the reflux condenser and slowly add 2 mL of 10% sodium bicarbonate solution, with stirring. Remove the aqueous layer, check its acidity with litmus paper, and discard as before. Repeat the procedure until the aqueous phase is no longer acidic to litmus.

b. Dehydration of the Silicone Fluid

Tare a 50 mL beaker.

Prepare a short drying and chromatography column as follows. Place a plug of Pyrex wool at the bottom of a 25 mL buret, then add a layer of about 3/4" of silica gel. Place about 3/4" of anhydrous sodium sulfate atop the layer of silica gel.

Carefully transfer the wet ether solution of silicone fluid to the top of the column. Open the column outlet and begin collecting the eluate in the tared 50 mL beaker. If the rate of flow of the solution is too low, place a rubber thermometer adapter atop the column, then use a pipet bulb fitted with a plastic pipet tip to apply pressure to the column. When the liquid layer has almost reached the top of the column, add an additional 6 mL of ether. Continue collection of the eluate until a further 4 mL has collected.

c. Cross-Linking of the Silicone Fluid

IN THE HOOD (Watch out for flames!), evaporate the ether on a steam bath or hot plate. This will leave a residue of silicone fluid. Weigh the flask plus product, then add an amount of boric acid which corresponds to ca. 5% of the weight of the product. Stir for about five minutes with a spatula.

Heat the mixture to ca. 170-180°C on a sand bath until a stiff gum is obtained. This should occur within about 20 minutes. Allow the gum to cool to room temperature.

Remove the product from the flask and, if it is brittle, knead it until it becomes pliable. Test it for: (1) bouncing properties; (2) behavior when stretched slowly; and (3) behavior when stretched rapidly.

Report

1. Calculate the yield of polymer from $(CH_3)_2SiCl_2$. For purposes of calculation, assume a polymeric composition of approximately $[(CH_3)_2SiO]_n$ (i.e. empirical formula C_2H_6SiO).
2. Obtain an infrared spectrum of the polymer and assign the bands due to (a) C-H stretching, and (b) Si-O stretching.

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[1] Adapted from the procedure given in Microscale Inorganic Chemistry, Z. Szafran, R. M. Pike, and M. M. Singh, John Wiley & Sons, New York, 1991.

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PRE-LAB QUESTIONS

1. Why is it possible to approximate the formula of a polymer $HO\text{-}(SiR_2O)_nSiR_2\text{-}OH$ by the formula SiR_2O?

2. Write a balanced equation for the end-capping of a polymer $HO\text{-}(SiR_2O)_nSiR_2OH$ with chlorotrimethylsilane.

3. Write a balanced equation for the reaction of boric acid with methanol to form trimethyl borate (the trimethyl ester of boric acid).

4. Show why the reaction of boric acid with the living silicone polymer results in cross-linking, rather than simple head-to-tail linking of the silicone chains.