CH 431 –Inorganic Chemistry

Experiment 5: Silicone Polymers

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Abstract

The purpose of this experiment was to synthesize a $(CH3)_2SiO$ polymer from $(CH3)_2SiCl_2$. Once synthesized, the product was putty-like and exhibited both solid and liquid like properties. The compound was synthesized successfully, and the percent yield of the reaction was 114%. This was attributed to residual ether left in the flask when measurements were taken. The mass of the final product was 5.147 g.

Introduction

The purpose of this experiment was to synthesize a silicone $(CH3)_2SiO$ polymer from dimmethyldichlorosilane ($(CH3)_2SiCl_2$). Polymers are large molecular weight molecules composed of repeating units of smaller monomers. Their repeating structure was first recognized and proposed by Hermann Staudinger in the 1920's.[1] Polymers can be found naturally occurring in nature such as natural rubber being harvested from trees.

Polymers can also be created synthetically through the use of many different mechanisms like step-growth, chain-growth, or free-radical polymerization. Polymers can be found in a wide array of consumer products such as tires, soda bottles, CD cases, and coffee cups.[2]

Silicones, or polysiloxanes, are polymers than contain alternating silicone and oxygen atoms. Silicones were commercialized in the 1940's due to the work of Hyde and Rochow.[3]

These polymers are versatile, and can be used in a variety of products including glass, plastics, and viscoelastic rubbers.[4]

The silicone polymer synthesized in this lab behaves as a viscoelastic material. This means that the polymer exhibits properties of both a viscous fluid and an elastic solid. The viscosity and properties of these materials are time dependent. For example, when silly putty is stretched, or deformed over a large time scale, it flows like a fluid, but when it is dropped, or deformed over a short time scale, it bounces like an elastic solid.

The synthesis of the liquid polymer was carried out according to the following reaction.

$$n\,[Si(CH_3)_2Cl_2] + n\,H_2O \rightarrow [Si(CH_3)_2O]_n + 2n\,HCl \qquad (1)$$

The liquid polymer was then reacted with boric acid to create the final product. This reaction is illustrated in the results section.

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Experimental Method, Calculations, and Yield

This experiment involved the use of dimethyldichlorosilane, diethyl ether, sodium bicarbonate, magnesium sulfate, and boric acid. These chemicals are potentially harmful if ingested, inhaled, or contacted. To prevent this, gloves, lab coats, and safety goggles were worn during the entire lab period. All liquid chemicals were measured and poured in the fume hood to decrease the risk of inhalation. Due to the creation of HCl vapors during the reaction, the synthesis itself was also performed in the fume hood. In addition, diethyl ether has a low flash point, so heating was done slowly to prevent fire hazards.

To synthesize the polymer, 40 mL of diethyl ether and 20 mL of dimethyldichlorosilane were added into a flask. 40 mL water was added slowly using a pipette to control the reaction

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temperature and vapors. The solution was separated using a separatory funnel, and then the ethereal layer was washed with a sodium bicarbonate solution to neutralize the mixture.

A second washing was performed with water, and then the mixture was dried using anhydrous magnesium sulfate and filtered. The mixture was heated on a hot plate to evaporate off any remaining ether. The volume of liquid polymer at this point was about 15 mL. Finally, boric acid was added to the liquid polymer while heating at 120°C to produce the final polymer. The final mass was 5.147 g.

The percent yield for this reaction was calculated using the following calculation. The average density used for the polymer chain was 0.960 g/mL.[5]

$$Theoretical\ Yield = (20\ mL\ (CH_3)_2SiCl_2)\left(\frac{1.06\ g}{mL}\right)\left(\frac{mol}{129.06\ g}\right)\left(\frac{1\ mol\ repeat\ unit}{1\ mol\ reactant}\right)\left(\frac{74g}{repeat\ unit}\right) = 12.16\ g$$

$$Actual\ Yield = (15\ mL)\left(\frac{0.960g}{mL}\right) = 14.4\ g$$

$$Percent\ Yield = \frac{14.4\ g}{12.6\ g} \times 100\% = 114\%$$

The calculated percent yield was larger than physically possible, and this indicates that there was residual ether left in the flask when the measurement was taken.

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Results and Discussion

Once synthesized, the product was putty-like and exhibited both solid and liquid like properties. In this lab, $(CH_3)_2SiCl_2$ was easily hydrolyzed while $(CH_3)_2CCl2$ was not. This can be explained because Si has a larger atomic radius than carbon. A larger atomic radius leads to greater interaction with the d-orbitals of the molecule, and this leads to a higher reactivity with ligands. Therefore, it is easier for an H_2O ligand to attach to the Si molecule, which allows for easier hydrolysis.

The polymer solution was washed with sodium bicarbonate during washing and separation. This is due to the HCl by-product produced during the addition of water. To remove any remaining acid, a basic sodium bicarbonate solution is added to react with the acid and neutralize the solution.

Boric acid is added to the reaction mixture in the final step in order to crosslink the polymer further. Increasing the crosslink density causes the polymer to become stronger and exhibit different polymer properties. The initial polymer liquid has residual hydroxyl groups which can react with the boric acid to form Si-O-B bonds. Boric acid is trifunctional and, therefore, is capable of creating a large number of crosslinks within the polymer. This crosslinking allows for the formation of the putty like substance.[6]

The addition of the boric acid to the liquid polymer is illustrated below.

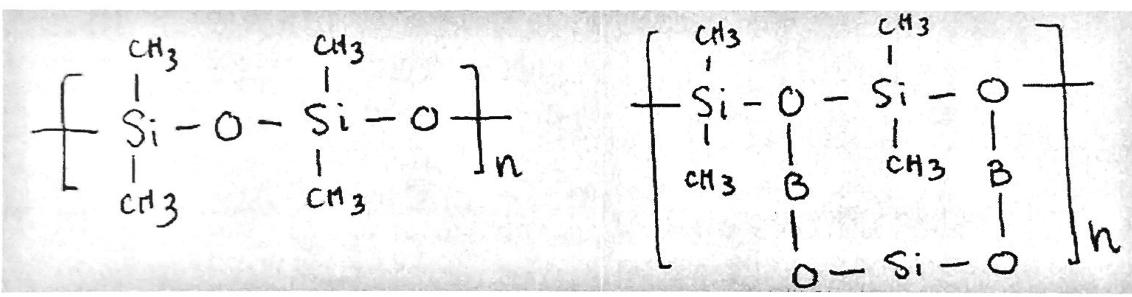

Figure 1. Initial structure of polymer (left) and final structure (right) once reacted with boric acid

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Conclusion

It can be concluded that the silicone polymer was synthesized successfully based on its viscoelastic properties. The percent yield of the experiment was 114%. This was attributed to residual ether left in the flask when measurements were taken.

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